to the article "Time-resolved CIDNP: an NMR way to determine the EPR parameters of elusive radicals" by Olga B. Morozova, Konstantin L. Ivanov, Alexey S. Kiryutin, Renad Z. Sagdeev, Talea Köchling, Hans-Martin Vieth, Alexandra V. Yurkovskaya

To get an idea on the applicability of the simple proportionality relation between CIDNP intensities and HFCCs we performed numerical simulations assuming different numbers of magnetic nuclei in the system and an analytical treatment of the problem under consideration.

Numerical simulations of CIDNP at high fields

To obtain an idea on the validity and applicability range of the proportionality relation, at first, we performed numerical calculations of CIDNP in radical pairs with different numbers of magnetic nuclei. To check the proportionality relation we ran simulations for different numbers of magnetic nuclei of in radical pairs and assumed that the HFCCs took random values in the range of [-1 mT; 1 mT] and varied the number of nuclei, *N*. The value of δ was varied in a wide range, so that the situations of comparable HFCC and $\delta = \Delta g \mu_B B$ terms and $\delta \gg$ HFCC term were also covered by our treatment. For the calculations Adrian's model (see main text of the article) was used.

The results of the calculation are presented in Figure S1. We plotted the calculated CIDNP values versus the randomly taken HFCCs and also performed fitting by a linear function CIDNP=C·HFCC. It is clearly seen that for small N (namely, for 3 and 4) the deviations from proportionality are so large that obviously the simple relation CIDNP \propto HFCC is not fulfilled. However, as N becomes larger the accuracy of the relation becomes noticeably higher: at N=6 the coefficient of determination is 0.97 for the proportionality relation. The coefficient of determination is roughly equal to unity minus square of the deviation, S^2 , thus, $R^2=0.99$ corresponds to roughly 10 % deviation; whereas $R^2=0.9999$ gives only 1% of deviation. At N=10 the proportionality relation CIDNP=C·HFCC already very well describes the dependence. If a different set of random HFCC values is taken the same tendency is seen: for small N no proportionality exists, for N>5 the proportionality relation becomes quite accurate, whereas for N>10 it is perfectly fulfilled.



Figure S1. Calculated dependencies of high-field CIDNP of HFCC for 3 (a), 4 (b), 6 (c) and 10 (d) magnetic spin 1/2 nuclei. The HFCCs take random values in the range [-1 mT;1 mT], δ =0.5 mT. Solid lines show the best fits with linear functions $P_i = Ca_i$; coefficients of determination, R^2 , are given for all subplots.

Figure S2 shows the coefficients of determination, R^2 , for the proportionality relation for different numbers of nuclei N and different values of the parameter $\Delta g \mu_B B / a_{max}$, for each N and $\Delta g \mu_B B / a_{max}$ ten different random sets of HFCCs were taken. Apparently, the relation becomes valid not only when is large but also with an increasing number of nuclei. For instance, once N=10 the relation works well even for values, which are smaller than a_{max} and much smaller than the total HFC of all nuclei (width of the EPR spectrum of the radical pair). The solid lines modeling the CIDNP dependence on the number of nuclei and the value of δ are discussed later in the text.

Keeping in mind the fact that in CIDNP experiments the accuracy of determining the net CIDNP is often not better than 5 %, we conclude that even the data obtained for N>5 can be used for the proportionality relation between CIDNP and HFCCs. Thus, this simple analysis indicates that the relation is fulfilled for a sufficiently large number of nuclei or, alternatively, for a large term, which is a rather unusual situation for pairs of organic radicals. However, its origin and precision are still open as it does not follow obviously from the general expressions, eqs. (1-3), because the HFC terms do not contribute linearly to the result for CIDNP. Moreover, for a small number of nuclei even

Kapsen Morrish Ellion PCB may break down as it is known from the work by Salikhov¹. To

clarify these questions let us tackle the problem analytically.



Figure S2. Dependence of the coefficient of determination, R^2 , for the proportionality relation on the parameter $\Delta g \mu_B B/a_{max}$ as calculated for different number of magnetic nuclei, N, in the radical pair. Method of calculation is the same as for Figure S1; for each N and $\Delta g \mu_B B/a_{max}$ value ten random HFC configurations were taken. Solid lines represent function $1 - \alpha S^2$ with $S^2(x,N)$ taken from eq. (S6).

Analytical considerations of CIDNP in multi-nuclear systems at high magnetic fields

Let us obtain analytically the criterion for proportionality and derive deviations from this relation.

To do so, let us present the rate of inter-system crossing in the same way as in eq. (4)

$$\omega(M_1,...,M_N;M_1,...,M_N) = \frac{1}{2} (\delta + a_1 M_1 + A_1)$$
(S1)

with A_1 being the HFC term of the set $\{2, ..., N; 1, ..., N'\}$ of nuclei (all nuclei except for the first one); similarly, A_i is the HFC term of all nuclei except for the *i*-th one:

$$A_{i} = \sum_{k=1,k\neq i}^{N} a_{k} M_{k} - \sum_{j=1}^{N'} b_{j} M_{j}$$
(S2)

Let us assume for the moment that $|a_1M_1| << |\delta + A_1|$. The limits of such assumption will be established later. In this approximation the expression for P_1 can be rewritten as follows:

Here summation is taken over all A_1 values, i.e., over the states of $\{2, ..., N; 1, ..., N'\}$ nuclei. Thus, if for a given state $|a_1M_1| << |\delta + A_1|$ this state will give a contribution to P_1 , which is proportional to a_1 . This is the origin of the sought proportionality relation. However, there are still a few points that need to be clarified, namely, the validity of the approximation used in eq. (S3) and under what conditions $C_i = C$ for any *i*.

The inequality $|a_1M_1| \ll |\delta + A_1|$ is obviously fulfilled when the δ term is much larger than the HFC term, as has been shown earlier ². In this case the Taylor series expansion can be used with the small parameter being $(a_1M_1+A_1)/\delta$, which rather obviously leads to CIDNP \propto HFCC. A similar situation is met if there is a nucleus in the spin system with a HFCC that is much larger than the rest of the HFC term. Then for all other nuclei proportionality $(P_i \propto a_i)$ is expected. However, from our previous study³ and the preceding numerical analysis it is known that the relation $P_i \propto a_i$ has a much broader applicability range. Let us consider the problem in more detail restricting it to the same situation as in the numerical modeling of CIDNP. The HFCCs, a_i and b_j , are assumed to take random values from $-a_{max}$ to a_{max} . In the situation chosen we will compare the HFCC, a_i , of an individual nucleus with the effective HFCC of all other nuclei, A_i , and find out under what conditions $a_i \ll A_i$ holds and the coefficients C_i coincide. The term A_i defined in eq. (S2) is a random quantity and its normalized distribution, $f(A_i)$, is Gaussian in accordance with the central limiting theorem (distribution of N+N'-1 independent random quantities):

$$f(A_i) = \frac{1}{\sqrt{2\pi(N+N'-1)\sigma^2}} \exp\left(-\frac{A_i^2}{2(N+N'-1)\sigma^2}\right)$$

= $\frac{1}{a_{\max}} \sqrt{\frac{3}{2\pi(N+N'-1)}} \exp\left(-\frac{3A_i^2}{2(N+N'-1)a_{\max}^2}\right).$ (S4)

Here $\sigma^2 = a_{\text{max}}^2 / 3$ is the dispersion of the distribution of the quantity $a_i M_i$. The approximation used in eq. (S3) cannot be fulfilled for all possible A_i values in the distribution $f(A_i)$, namely, it is violated for those A_i that $|a_1M_1| > |\delta + A_1|$, otherwise it is valid. Thus, for rather small δ values there are always A_i Supplementation Matrich (ESM) fait FGCP(S3) breaks down. The problem of justifying the proportionality relation thus transforms into the task of elucidating under what conditions the statistical weight of the events $|a_iM_i| > |\delta + A_i|$ is small enough. Indeed, if such weight is sufficiently small then $P_i = C_i a_i$ holds, moreover, $C_i = C_j = C$ for any *i* and *j*, and the proportionality between CIDNP and HFCC is fulfilled with high accuracy. The weight of "unwanted" A_i values (so that $|a_iM_i| > |\delta + A_i|$) is given by integration of the distribution $f(A_i)$ from eq. (S4) from $(-\delta - a_i/2)$ to $(-\delta + a_i/2)$. This integral can be roughly estimated as the area of the corresponding trapezoid:

$$S \approx \frac{|a_i|}{a_{\max}} \sqrt{\frac{3}{2\pi(N+N'-1)}} \exp\left(-\frac{3\delta^2}{2(N+N'-1)a_{\max}^2}\right).$$
 (S5)

The condition *S*<<1 guarantees the proportionality between the CIDNP of the nucleus and its HFCC at the radical stage of the reaction: $P_i = Ca_i$. More generally, for arbitrary HFCCs the simple relation $P_i = Ca_i$ holds if $a_i \cdot f(A_i = -\delta) <<1$ (which is approximately the integral of $f(A_i)$ from $(-\delta - a_i/2)$ to $(-\delta + a_i/2)$). The square of the deviation from proportionality is given by S^2 . If we assume that a_i and a_{max} are of the same order of magnitude then approximately

$$S^{2}(x, N+N') \approx \frac{3}{2\pi(N+N'-1)} \exp\left(-\frac{3x^{2}}{(N+N'-1)}\right)$$
 (S6)

where $x = \delta/a_{\text{max}}$. The function given by eq. (S6) well describes the deviations from proportionality presented in Figure S2. As it is seen, the solid lines representing the dependence $R^2 = 1 - \alpha \cdot S^2$ (α is the coefficient used here as the fitting parameter) are in good agreement with the data of the numerical "experiment".

The value of the weight of "unwanted" HFC configurations is illustrated by Figure S3. This weight is given by the area of the shaded part of the normalized Gaussian $f(A_i)$. To ensure small area of this part either should be small (integration is performed over the far wings of the distribution) or the width of the Gaussian should be much larger than the individual HFCCs. For fixed N+N' the deviation decreases exponentially with increasing x^2 . However, even if |x|<1 (i.e., δ is smaller than or comparable to a_{max}) a large number of nuclei, N+N', may make the deviation from the

profit of the owner societies 2011 speaking, with increasing N+N' and small x values the deviation S^2 decreases as 1/(N+N'-1). In general, the proportionality relation is fulfilled for every nucleus, whose HFCC is much smaller than the total width of the EPR spectrum of the rest of the nuclei. Fulfilling this condition guarantees the proportionality relation.



Figure S3. Normalized Gaussian distribution, $f(A_i)$, of the A_i term illustrating the weight of "unwanted" HFC configurations for different number of magnetic nuclei in the system. Shaded area shows the part of the distribution corresponding to the unwanted spin configurations.

Correlation of the CIDNP intensities of TCBP with the known HFCCs of the anionic radicals of TCBP for different reactants

For testing the theory and for determination of HFCCs of different radical the geminate CIDNP spectra were obtained during photoreactions of 3,3',4,4'-tetracarboxybenzophenone (TCBP) with different quenchers, namely, L-tyrosine, L-tryptophan, L-histidine, methionine-glycine, N-acetyl tyrosine, and N-acetyl tryptophan (the data for N-acetyl derivatives were not included into the main manuscript; here, they are used for additional illustration). The plotted CIDNP intensities of TCBP signals versus the known HFCCs for TCBP anion radical give linear dependencies (shown in Figure S4) which are assembled into two columns: the one on the left hand side represents the data with coefficients of determination, R^2 of 0.999 or higher (plots a, b, c). The data in the column on the right hand side have R^2 of 0.999 and lower (plots d, e, f), with a characteristic pattern in the plot. The first group was obtained for the photoreaction of TCBP with L-tryptophan and its N-acetyl derivative, and with the peptide Met-Gly, for which the mechanism of quenching of triplet excited states is electron transfer.^{4, 5, 6} Therefore, for these quenchers the formation of the TCBP radical anion was established, which was confirmed by the very high coefficient of determination in the dependencies of CIDNP on the known HFCCs of the TCBP radical anion. For tyrosine and histidine,

which presentates Mathematical ESD for PGFBup of the data obtained, under our experimental conditions the mechanism of triplet quenching is hydrogen transfer.⁶⁻⁸ In our case, this reaction mechanism leads to the formation of the TCBP ketyl radical, which is likely to have HFCCs different from those in the TCBP radical anion. Thus, comparing the plots from the left column (a, b, c) and from the right column (d, e, f) we conclude that the latter refer to the TCBP ketyl radical. The HFCCs for this radical were determined using the known HFCCs of the tyrosyl radical, and are listed in Table I of the manuscript.



Figure S4. Correlation of the geminate ¹H CIDNP intensities of 3,3',4,4'-tetracarboxybenzophenone (TCBP) in the photoreaction of TCBP and L-tryptophan (a), L-methionine-L-glycine (b), N-acetyl tryptophan (c), L-tyrosine (d), L-histidine (e), and N-acetyl tyrosine (f) with the HFCCs of the protons of the TCBP radical anion. Solid lines - the best fit by the function $P_j = -Cb_j$.

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