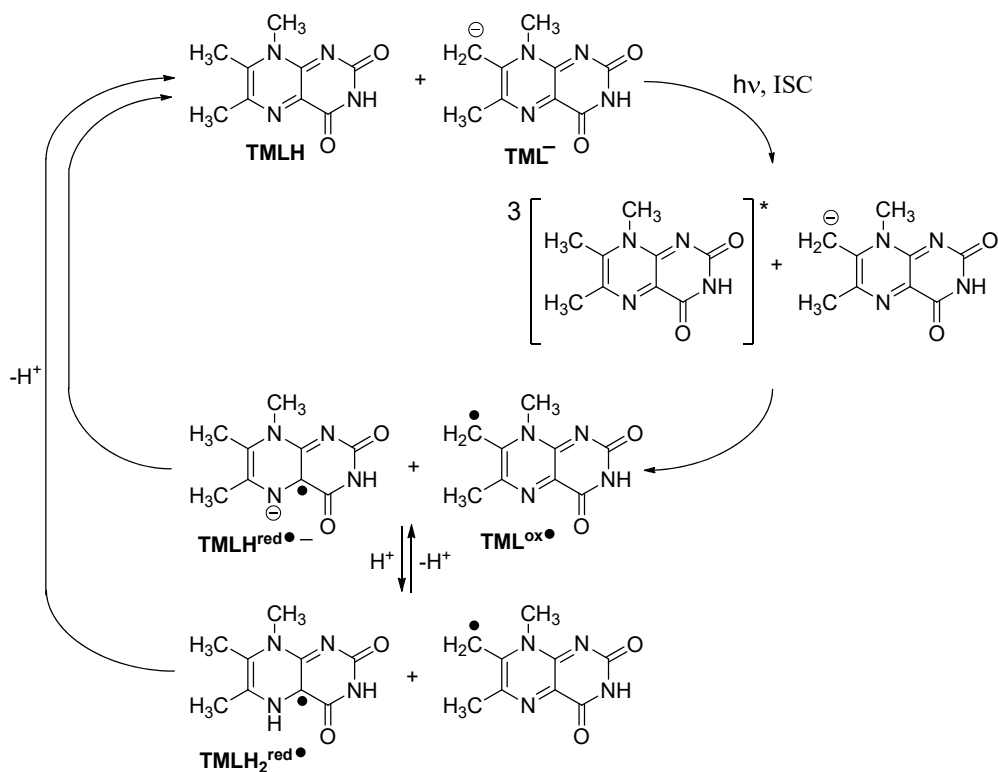


The manuscript “Non-classical disproportionation revealed by photo-CIDNP NMR” by Weber and co-authors describes the results obtained by photo-CIDNP in the disproportionation reaction of the compound 3, called 6,7,8-trimethyllumazine in its triplet state with 6,7,8-trimethyllumazine in the ground state. The authors applied the pulsed variant of CIDNP detection with multiple repetition of a short laser pulse followed by an RF pulse for NMR detection.

In 2011 direct proportionality between individual amplitudes of geminate CIDNP and the corresponding hyperfine coupling constants in a multinuclear radical pair at high magnetic field was theoretically predicted by the brilliant scientist Konstantin Ivanov, who too early passed away on 05.03 2021. The linearity was explained and verified in the publication of Morozova, O. B.; Ivanov, K. L.; Kiryutin, A. S.; Sagdeev, R. Z.; Köchling, T.; Vieth, H.-M.; Yurkovskaya, A. V., Time-resolved CIDNP: an NMR way to determine the EPR parameters of elusive radicals. *Phys. Chem. Chem. Phys.* **2011**, *13* (14), 6619-6627. Prior to that, the Adrian model (F. J. Adrian, *J. Chem. Phys.*, 1971, *54*, 3918–3923) with a rather clumsy sum over all multiple nuclear spin projections was widely used for CIDNP simulation. Please, refer to these publications in the manuscript.

The results obtained are very interesting and the manuscript is written quite nicely. However, I agree with the comment of referee 1, that the general reaction scheme is needed to clarify the chemical processes in aqueous solution leading to CIDNP formation.

For the special issue dedicated to Prof. Robert Kaptein who remarkably contributed to CIDNP as a mature science, we decided to assist the authors of this nice manuscript and propose such a reaction scheme to show the process resulting in CIDNP formation. The scheme is shown below. In a reaction involving e-transfer coupled with proton transfer (PCET) between 6,7,8-trimethyllumazine in its triplet state and 6,7,8-trimethyllumazine in the ground state the primary triplet radical pair of ($\text{TMLH}^{\text{red}\bullet-}$ – $\text{TML}^{\text{ox}\bullet}$) is formed. It can either recombine or reversibly form ($\text{TMLH}_2^{\text{red}\bullet}$ – $\text{TML}^{\bullet\text{ox}}$) via protonation-deprotonation as shown in the scheme. On a second reaction path the radical pair disproportionates with formation of the same products (the arrow indicating the release of a proton ($-\text{H}^+$)), but with a different CIDNP pattern.



The resulting CIDNP pattern detected in the diamagnetic product of these reversible reactions is formed at least in two pairs. For each pair, the own proportionality relationship between HFCCs and CIDNP holds. For a similar situation, in the reaction of carboxy benzophenones, it was proposed to utilize a linear combination of proportionality relationships to find the share of several radical pairs that contribute to the CIDNP signal. (Morozova, O. B.; Panov, M. S.; Fishman, N. N.; Yurkovskaya, A. V., Electron transfer vs proton-coupled electron transfer as the mechanism of reaction between amino acids and triplet-excited benzophenones revealed by time-resolved CIDNP. *Phys. Chem. Chem. Phys.* 2018, 20 (32), 21127-21135). This procedure works very nicely for other cases as well (see examples in the recent paper “Molecular features toward high photo-CIDNP hyperpolarization explored through the oxidocyclization of tryptophan” *Phys. Chem. Chem. Phys.*, 2021, Advance Article <https://doi.org/10.1039/D0CP06068B>).

When applied to the reaction of the methylated lumazine the result is shown in figure 1 by the red line and red symbols. Indeed, the linear combination of two radical pairs with shares of 0.23 and 0.77 provides perfect linearity with $R^2=1$.

Moreover, the correct approach to proportionality of CIDNP vs HFCCs is to use one common normalization of CIDNP intensities for the whole CIDNP spectrum, but not different ones for individual patterns from different protonation forms as it is done in Table 2, and to combine proportionalities in a single plot (see Fig. 1). In this case, different slopes (that did not receive an explanation by the authors) are clearly seen making it easier to follow the corresponding discussion.

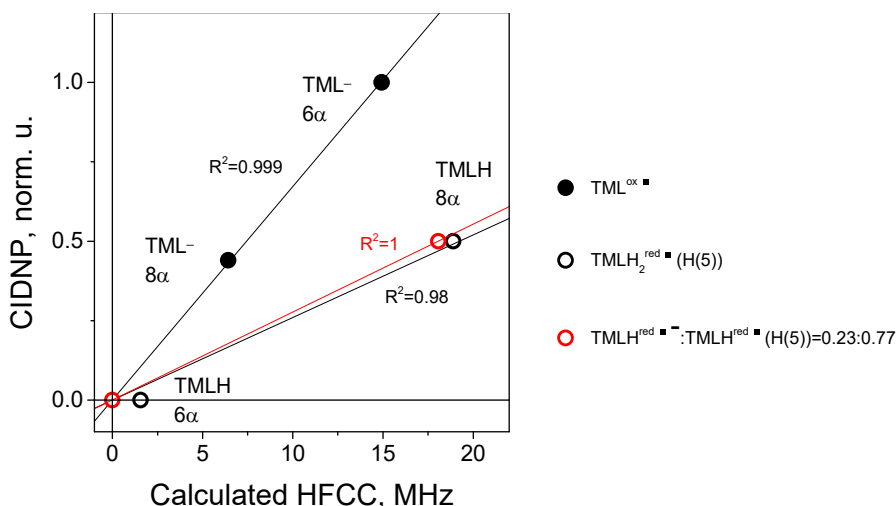


Figure 1. Correlation between calculated HFCCs of TML radicals, and CIDNP intensities of corresponding protons of TMLH and TML^- , detected during irradiation of TML solution. CIDNP intensities are multiplied by the corresponding $\text{sgn}(\Delta)$.

Such a way of presenting the experimental data makes the interpretation of CIDNP data very straightforward. Since the interconversion case by protonation and deprotonation for two radical pairs is revealed and explained in full accordance with the *classical* CIDNP theory proposed by Robert Kaptein, I strongly recommend to remove the word “non-classical” from the title or rephrase it. The CIDNP application to the studied reactions once again demonstrates the predictive power of CIDNP introduced by Prof. Robert Kaptein whose 80th anniversary we all celebrate!

The paper can be accepted after a revision as described above.