

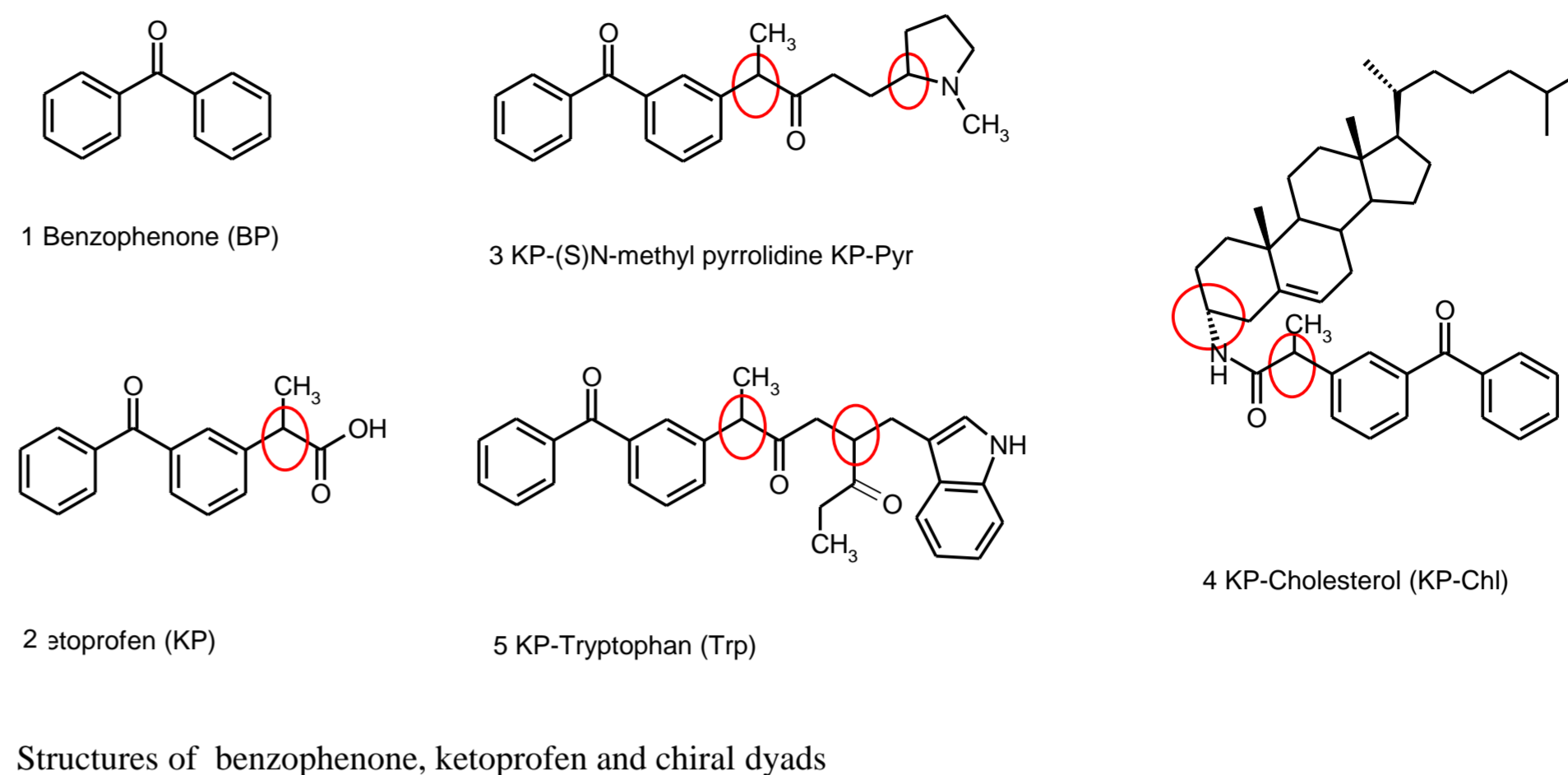
# Solid state photo-CIDEP in chiral linked systems

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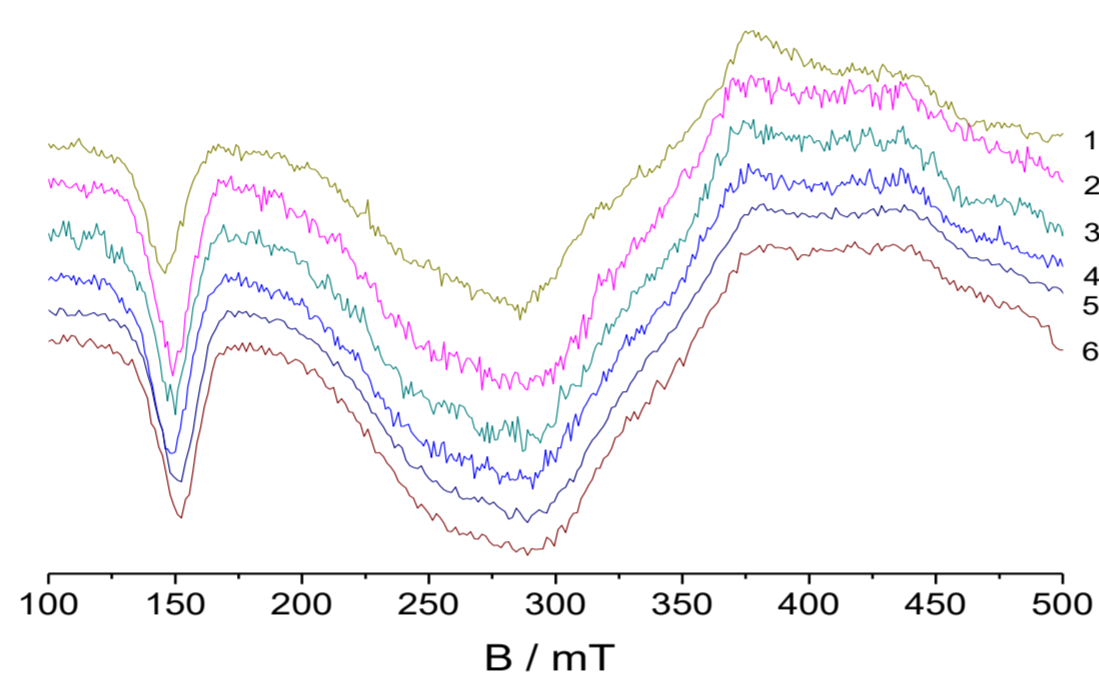
## Abstract

Photoinduced processes with charge transfer in diastereomers are currently being intensively studied as models for the binding of chiral drugs to chiral amino acid residues located in active sites of enzymes and receptors. So, direct detection of paramagnetic forms of diastereomers formed upon UV irradiation is of considerable interest. To detect paramagnetic particles formed as a result of the UV irradiation of dyads, containing the well-known NSAID (R/S) ketoprofen with several donors, we use a photochemically induced dynamic electron polarization (photo-CIDEP). The use of CIDEP allowed us to detect the triplet state of KP in all studied dyads in the solid state, as well as the product of intramolecular electron transfer in the dyad with tryptophan, (R/S)KP-(S)Trp, the biradical zwitterion (BZ) in solid and liquid states. The differences in the CIDEP spectra of the BZs of RS and SS diastereomers correspond to those predicted earlier based on the analysis of the CIDNP effects



## CIDEP of Triplet State

Previous studies by the methods of photochemistry and spin chemistry have shown that under UV irradiation of the solution of dyad 3, 4 and 5 the formation of KP in a triplet excited state occurs. Further in dyad 4 it is followed by an intramolecular HT, and a parallel ET and HT in dyad 3. Further, the dyads 3 and 4 undergo cyclization. On the contrary, for diastereomers of the dyad with tryptophan only reversible ET from tryptophan in the singlet excited state to the KP in the ground state takes place. Neither the CIDEP spectra, nor the decay times of the dyads 3, 4 and KP show significant differences. This allows us to conclude that the triplet state of the chromophore, KP, makes the dominant contribution to the TR EPR of dyads 3 and 4



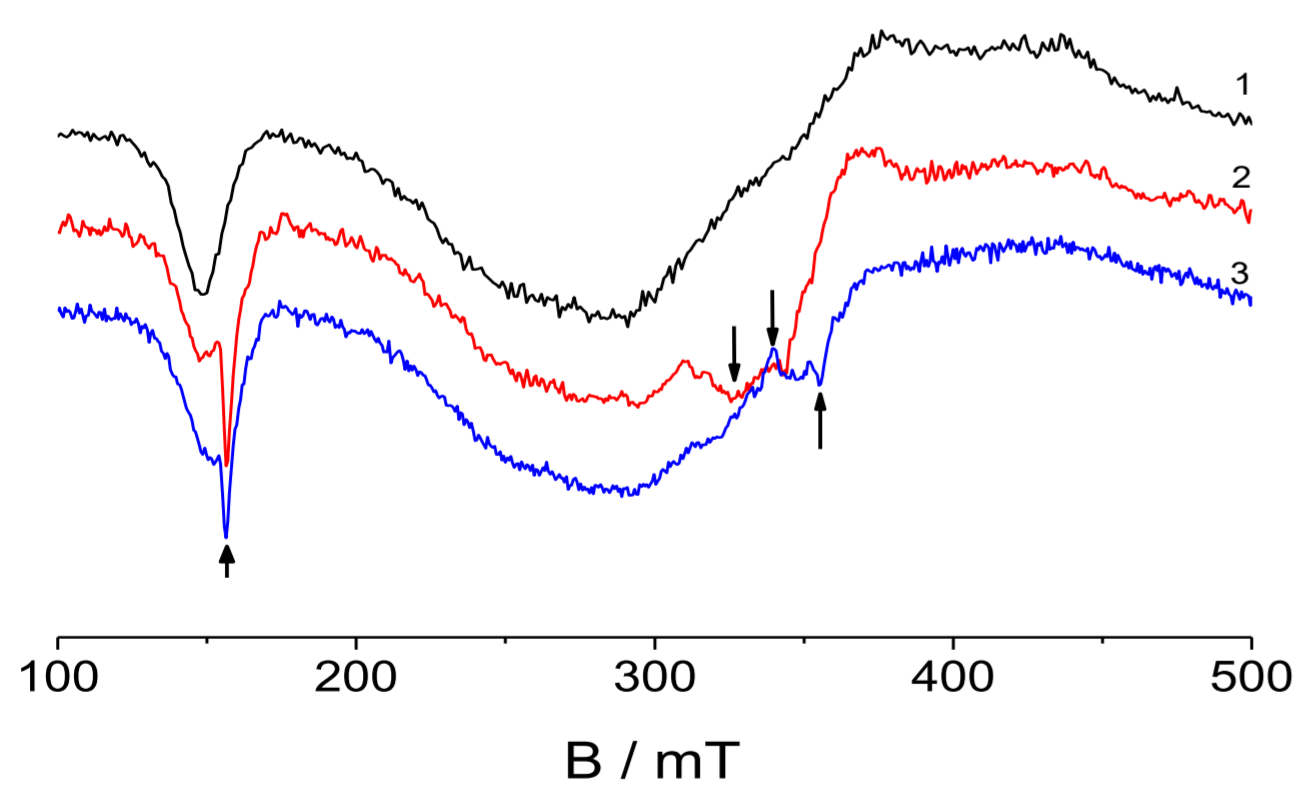
$\tau$ , $\mu$ s	149 mT	240 mT	286 mT	376 mT	433 mT
BP	1.7	1.7	1.8	1.9	1.6
KP	1.9	1.9	1.9	2	1.7
(S)KP-(S)Pyr	1.9	1.8	2	1.8	1.6
(R)KP-(S)Pyr	1.9	1.9	1.9	1.9	1.5
(S)KP-Chl	1.7	1.8	1.8	1.6	1.4
(R)KP-Chl	1.7	1.7	1.7	1.6	1.4
(S)KP-(S)Trp	1.0	1.14	1.35	1.0	1.0
(R)KP-(S)Trp	1.1	1.15	1.2	1.3	0.9

CIDEP spectra in toluene at 80-100K (excitation wavelength  $\lambda_{exc} = 355$  nm) and spectrum lines time decays of chromophores and dyads 1) BP, 2) KP, 3) racemate of (R/S)KP-(S)Pyr, 4) (S) KP-(S)Pyr, 5) (S) KP-Chl, 6) (R) KP-Chl.

## Additional CIDEP line

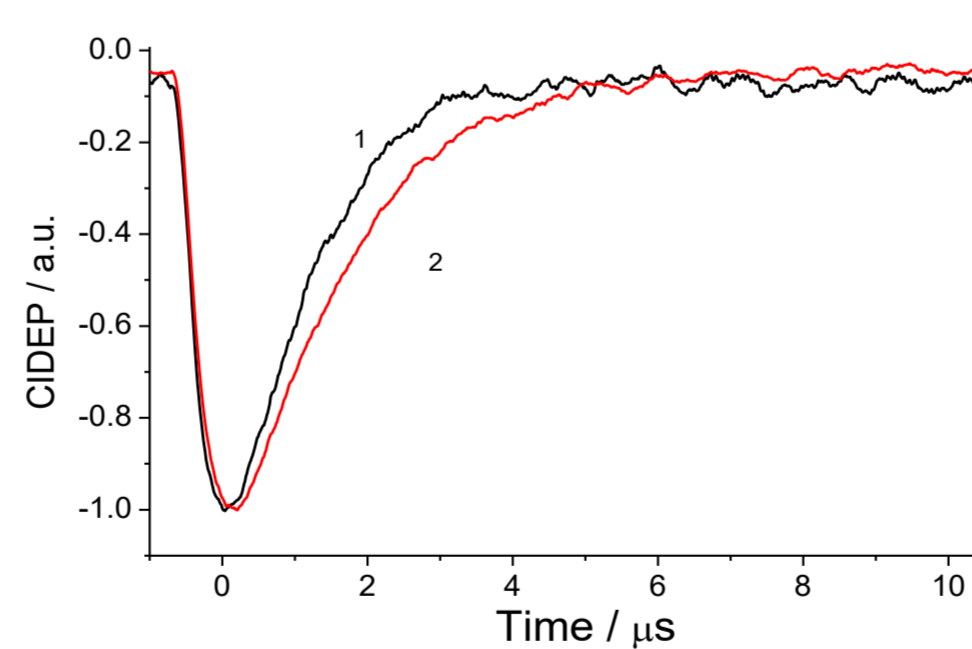
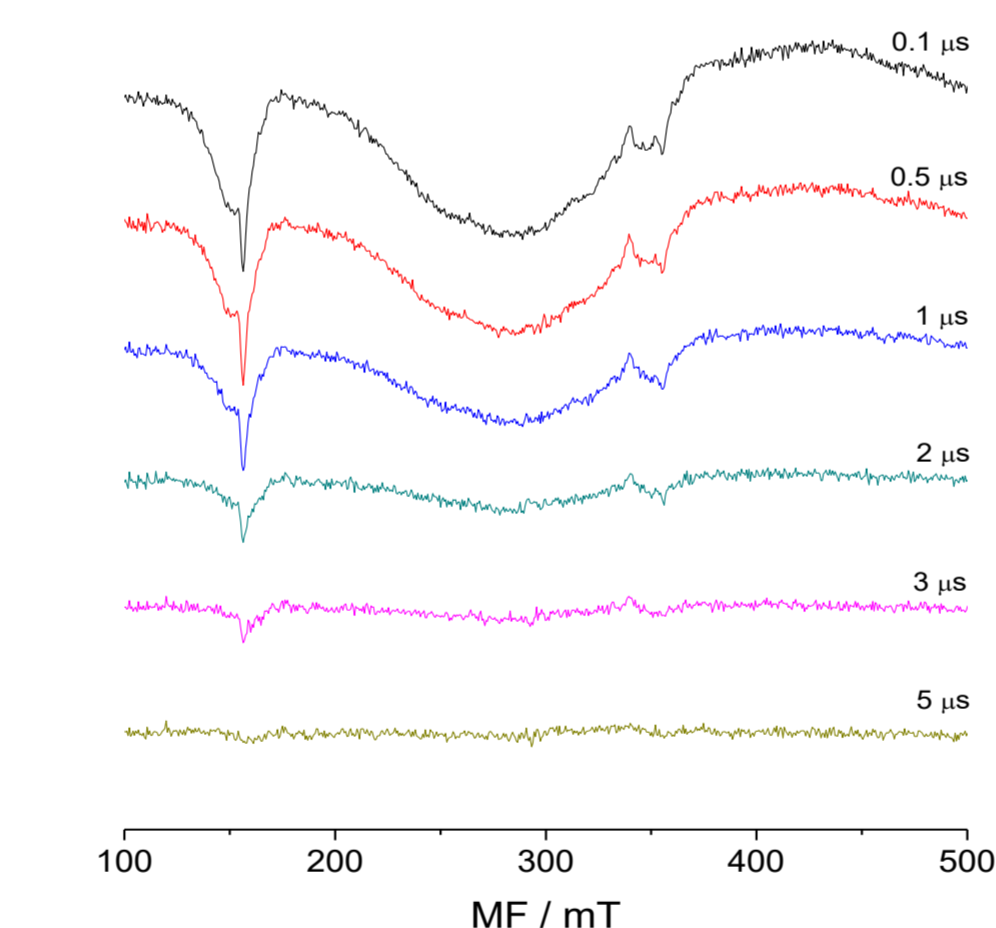
The spectra of the dyad with tryptophan, in addition to the spectrum of the KP triplet, demonstrate additional peaks that are absent in the dyad with N-methylpyrrolidine. The group of additional peaks is in the region of 350 mT. In the half-field, an additional signal is also observed, and it is shifted approximately by 10 mT from the corresponding signal of the KP triplet.

## Time dependence



CIDEP spectra in toluene glass detected at 80 - 100K. 1) (S) KP-(S)Pyr, 2) (R)KP-(S)Trp 3) (S)KP-(S)Trp. Arrows indicate well-defined lines which are absent in spectrum belonging to KP triplet.

$\tau$ , $\mu$ s	157 mT	340 mT	372 mT
(S)KP-(S)Trp	1.9	1.8	
(R)KP-(S)Trp	1.8		1.5



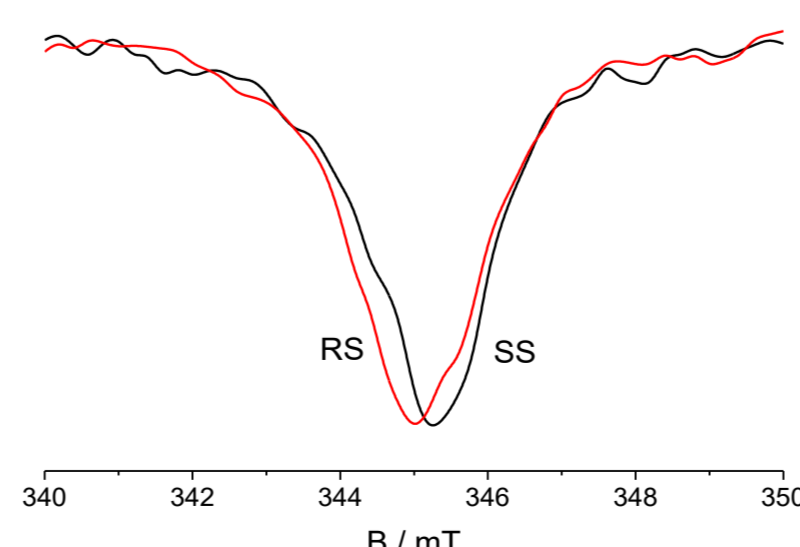
(S)KP-(S)Trp

(R)KP-(S)Trp

## Room Temperature

The CIDEP signal in dyad (R/S)KP-(S)Trp is also observed at a temperature of 280 K. The spectra feature are single lines with a width of about 1.9 and 2.0 mT for the RS and SS diastereomers, respectively, with decay times of about 0.45  $\mu$ s.

It is known that the photolysis of dyad 5(a,b) in solutions at room temperature results in formation of a BZ. Therefore, the TR EPR spectrum obtained can be confidently attributed to the BZ.



CIDEP spectra of (R)KP-(S)Trp and (S)KP-(S)Trp dyads in toluene at 280K

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**Declarations**

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