Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electron transfer vs proton-coupled electron transfer as the mechanism of reaction between amino acids and triplet-excited benzophenones revealed by time-resolved CIDNP

Olga B. Morozova,[a,b] Mikhail S. Panov,[a,b] Natalya N. Fishman[a,b] and Alexandra V. Yurkovskaya[a,b]*

[a]International Tomography Center, Institutskaya 3a, 630090 Novosibirsk, Russia

[b]Novosibirsk State University, Pirogova 2, 630090 Novosibirsk, Russia

Supporting Information

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Table S1. Calculated ^{1}H HFCCs of TCBP radicals of different structure.

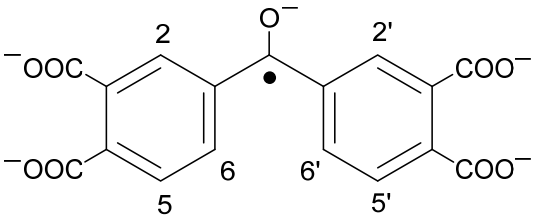
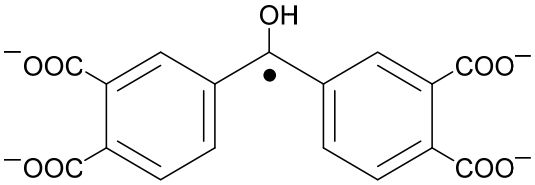
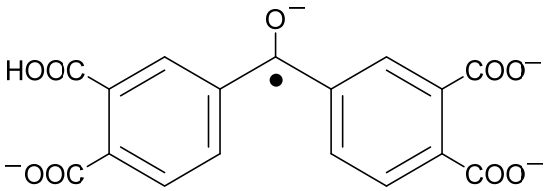
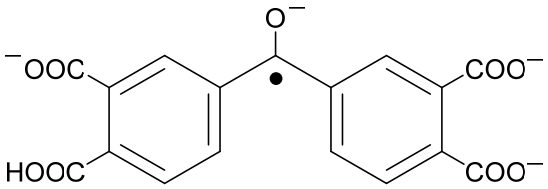
Radical			
T-I		H2	-0.304
		H2′	-0.287
		H6	-0.272
		H6′	-0.300
		H5	0.131
		H5′	0.141
T-II		H2	-0.455
		H2′	-0.383
		H6	-0.458
		H6′	-0.412
		H5	0.227
		H5′	0.217
		OH	0.086
T-III		H2	-0.134
		H2′	-0.178
		H6	-0.559
		H6′	-0.078
		H5	0.130
		H5′	0.056
		COOH	0.022
T-IV		H2	-0.219
		H2′	-0.094
		H6	-0.170
		H6′	-0.131
		H5	0.071
		H5′	-0.183
		COOH	-0.113

Table S2. Calculated ^{1}H HFCCs of DCBP radicals of different structure

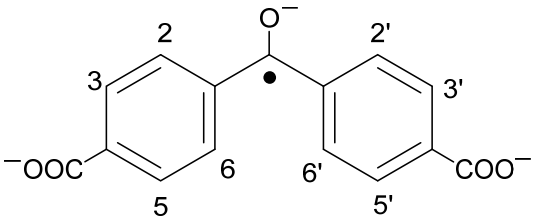
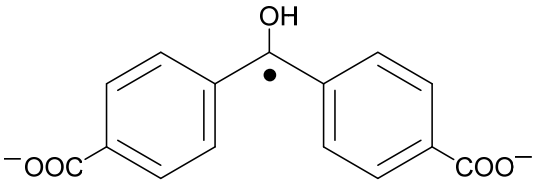
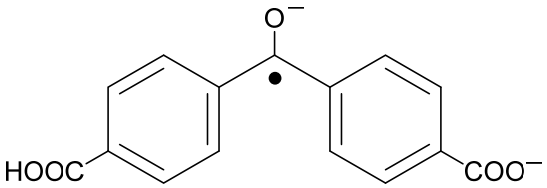
Radical			
D-I		H2	-0.270
		H2′	-0.272
		H6	-0.201
		H6′	-0.199
		H3	0.088
		H3′	0.089
		H5	0.037
		H5′	0.039
D-II		H2	-0.551
		H2′	-0.497
		H6	-0.544
		H6′	-0.509
		H3	0.299
		H3′	0.285
		H5	0.306
		H5′	0.282
		OH	-0.289
D-III		H2	-0.245
		H2′	-0.220
		H6	-0.194
		H6′	-0.192
		H3	0.002
		H3′	0.105
		H5	-0.056
		H5′	0.093
		COOH	-0.051

Table S3. Calculated ^{1}H HFCCs of 4-CBP radicals of different structure

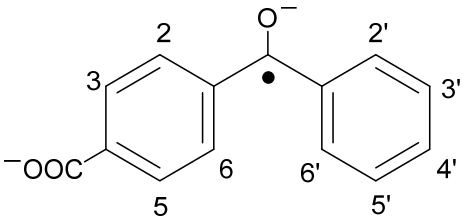
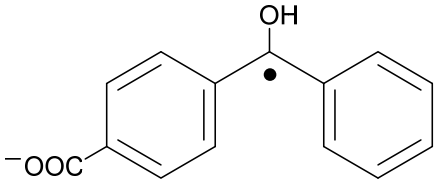
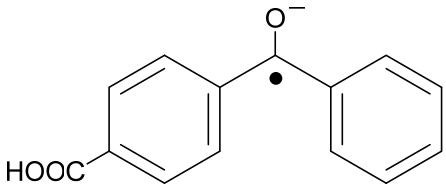
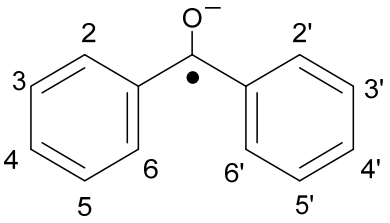
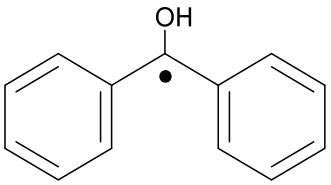
Radical			
4-I		H2	-0.387
		H2′	-0.343
		H6	-0.342
		H6′	-0.308
		H3	0.160
		H3′	0.162
		H4′	-0.390
		H5	0.146
		H5′	0.157
4-II		H2	-0.525
		H2′	-0.379
		H6	-0.515
		H6′	-0.396
		H3	0.237
		H3′	0.169
		H4′	-0.411
		H5	0.242
		H5′	0.168
		OH	-0.290
4-III		H2	-0.238
		H2′	-0.207
		H6	-0.161
		H6′	-0.170
		H3	-0.011
		H3′	0.077
		H4′	-0.234
		H5	-0.073
		H5′	0.066
		COOH	-0.050

Table S4. Calculated ^{1}H HFCCs of BP radicals of different structure

Radical			
I		H2,2′	-0.332
		H6,6′	-0.315
		H3,3′	0.127
		H4,4′	-0.419
		H5,5′	0.126
II		H2	-0.468
		H2′	-0.473
		H6	-0.460
		H6′	-0.479
		H3	0.199
		H3′	0.211
		H4	0.496
		H4′	0.522
		H5	0.200
		H5′	0.208
		OH	-0.305

Determination of HFCCs of DCBP anion radical

The photoreaction of DCBP with Trp which reacts with the excited triplets via electron transfer was used for experimental determination of the HFCCs of the DCBP radical anion. The tryptophanyl cation radical HFCCs, determined in our previos work [1], are given in Table S5 and were used as reference. The CIDNP spectrum obtained in photoreaction of DCBP and Trp is shown in Fig. S1. Enhanced absorption of protons H4 and H2, 6, and emission for protons H5 and β are in accordance with Kaptein's rules. Overlapping signals of H2, 6 and 5 were analysed together.

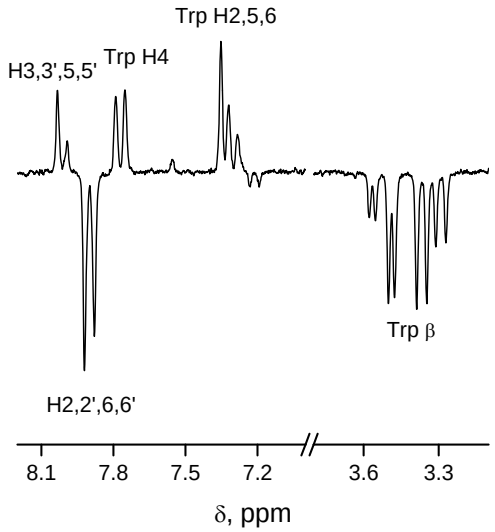


Figure S1. 200 MHz ^{1}H CIDNP spectra, obtained in the photoreaction of 0.5 mM 4,4´-dicarboxy benzophenone and 2 mM Trp in D_2O at pH 7.4.

The distribution of CIDNP intensities of Trp demonstrated a linear dependence on HFCCs with protons of tryptophanyl cation radical $Trp^{\bullet+}$ with determination coefficient R^2=1 (Fig. S2). Using the proportionality relation, we calculated HFCCs for DCBP radical anion **D-I** (Table 1,e): –0.25 mT (H2,2′,6,6′) and 0.075 mT (H3,3′,5,5′)

Table S5. ^{1}H HFCCs of tryptophanyl cation radical $Trp^{\bullet+}$ taken from Ref. 1.

Proton	HFCC, mT
H4	-0.45
H2,5,6	-0.19
α	-0.03
β	1.00

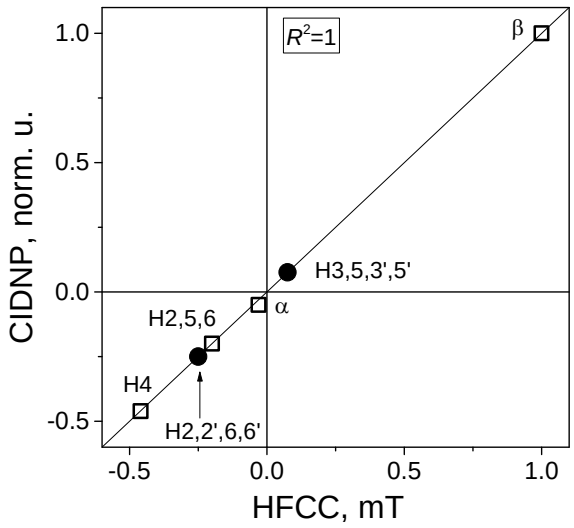


Figure S2. Correlation between the ^{1}H CIDNP intensities detected in the photoreaction of 4,4′-dicarboxy benzophenone (DCBP) and L-tryptophan (Trp), and the ^{1}H HFCCs of tryptophanyl cation radical $Trp^{\bullet+}$ (squares) and with DCBP anion radical **D-I** (circles). Solid line: best fit by the function $P_{2j}=-CA_{2j}$ (fitting to squares) with A_{2j} taken from Ref. 1 (Table S5); A_{1i} calculated from the dependence $A_{1i}=C^{-1}P_{1i}$ (fitting to circles).

References

[1] O. B. Morozova, K. L. Ivanov, A. S. Kiryutin, R. Z. Sagdeev, T. Köchling, H.-M. Vieth and A. V. Yurkovskaya, Phys. Chem. Chem. Phys., 2011, 13, 6619-6627