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Supporting Information

Application of W-band ^{19}F ENDOR Spectroscopy for distance measurement using trityl spin probe and fluorine

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X-band CW EPR spectra of compounds 1–5

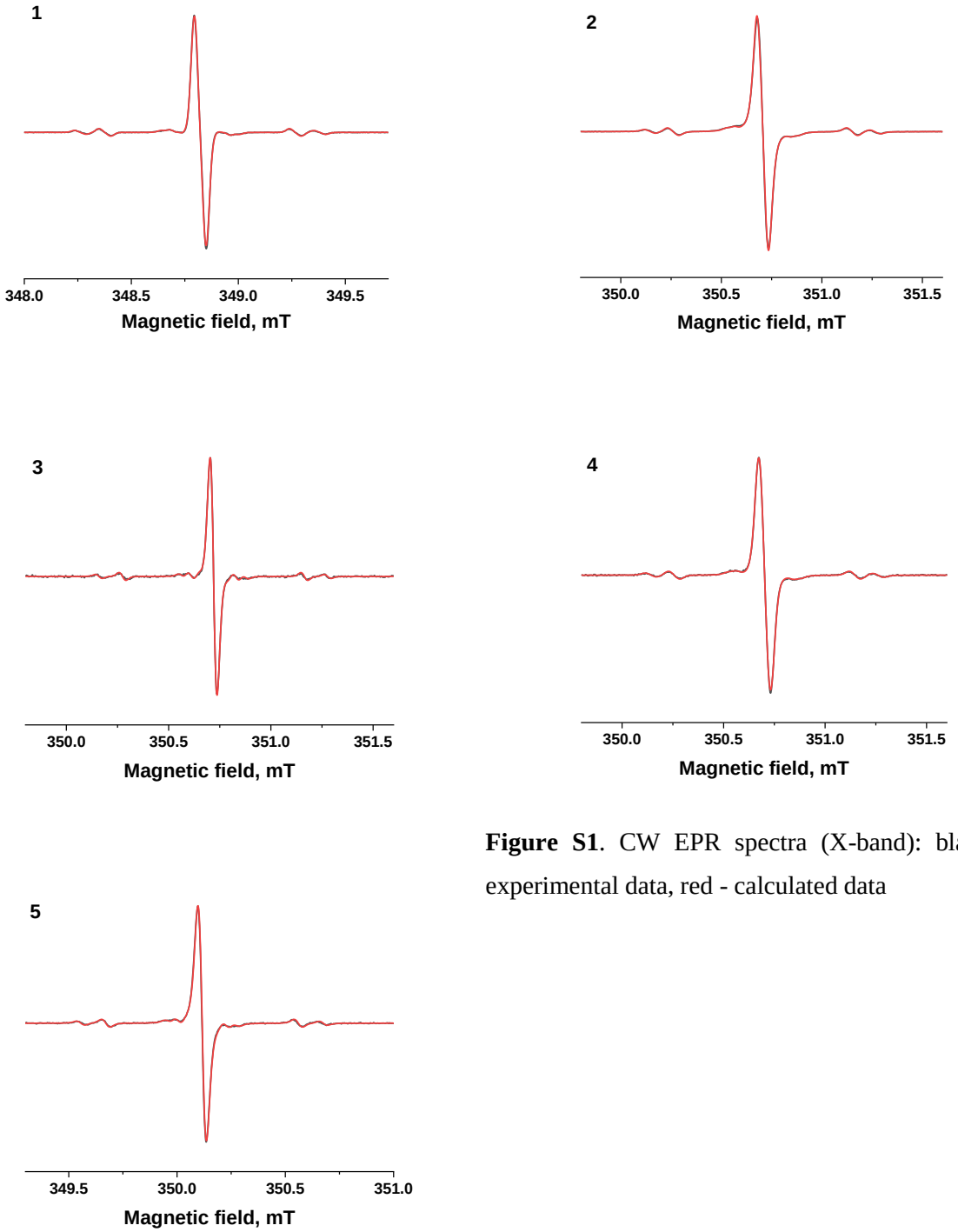


Figure S1. CW EPR spectra (X-band): black - experimental data, red - calculated data

Simulation parameters: g = 2.0032 ± 0.0004, satellites ^{13}C a = [1.12 0.89 0.31 0.22 0.12] mT. For compounds **1, 2**, and **4**, the *hfi* constant on ^{14}N was added. a_N = 0.018 mT.

W-band Echo–detected spectra of compounds 1–5

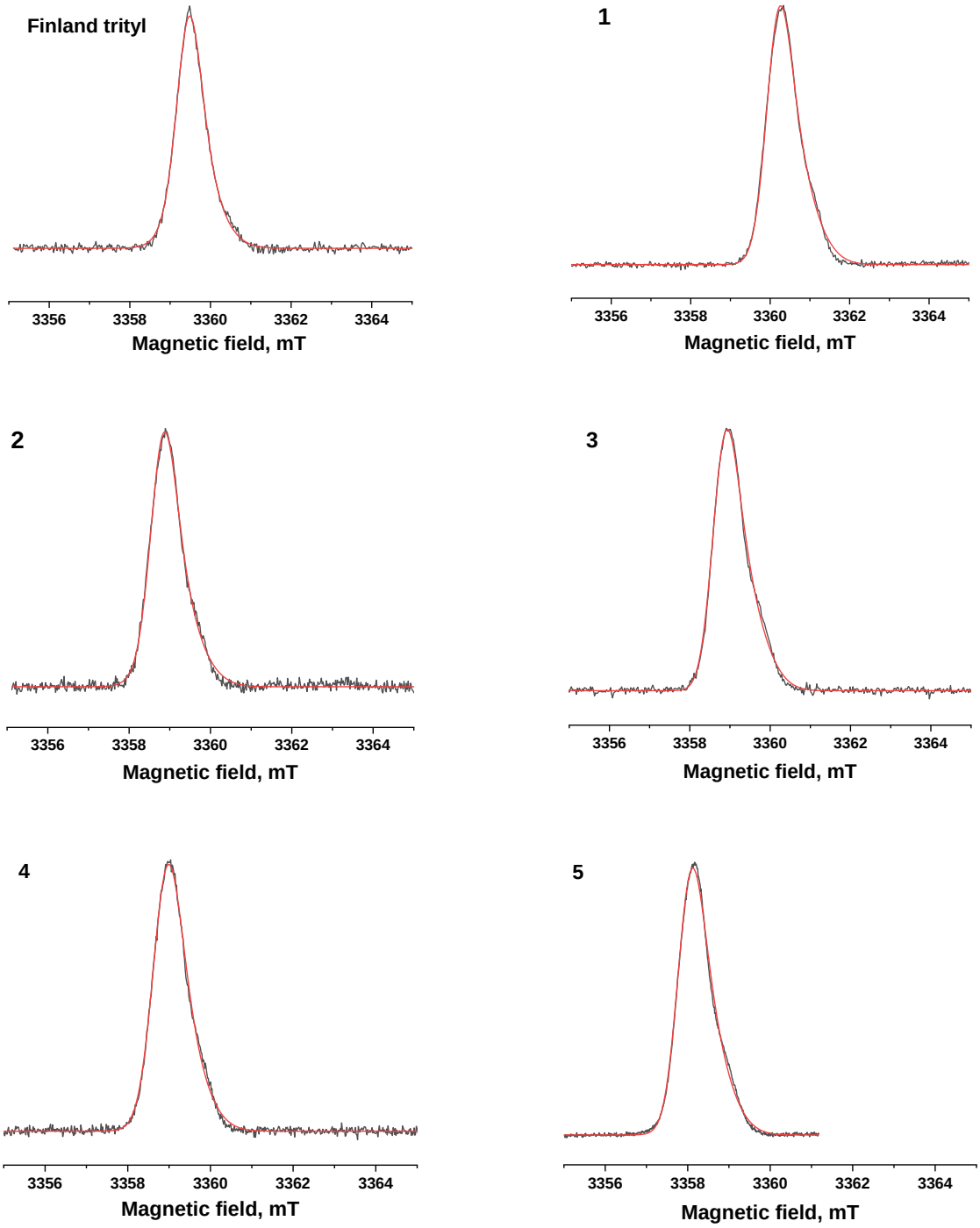


Figure S2. EPR spectra (W-band): black: experimental data, red: calculated data.

Table S1. The components of the g-factor for compounds **1–5**

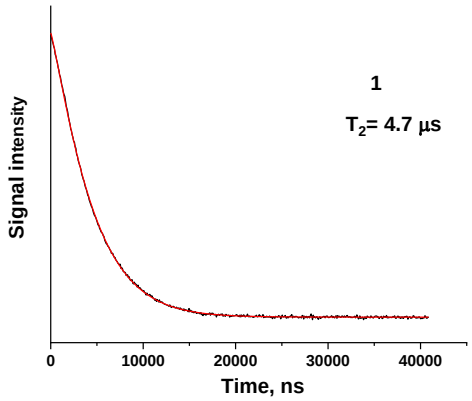
Sample	$g_{\perp}$	g_{II}	$g_{\perp} - g_{II}$	gStrain
Finland trityl	2.00353	2.00331	0.00022	0.0003 0.0009
1	2.00381	2.00334	0.00047	0.0004 0.0008
2	2.00363	2.00327	0.00036	0.0004 0.0009
3	2.00382	2.00329	0.00053	0.0004 0.0008
4	2.00377	2.00338	0.00039	0.0004 0.0008
5	2.00379	2.00330	0.00049	0.0004 0.0008

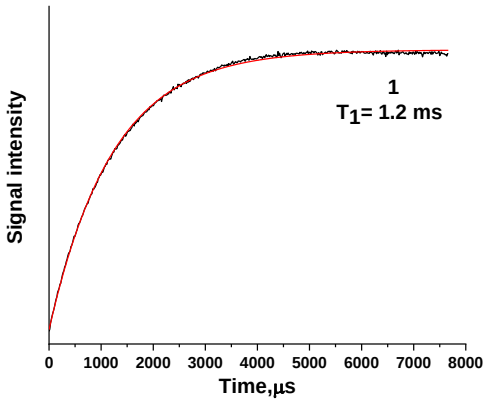
Relaxation measurements for compounds 1–5

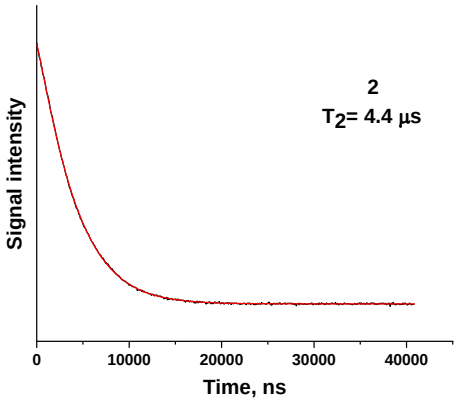
Experimental data on spin-lattice relaxation (T_1) and phase relaxation (T_2) were processed by means of the following mono-exponential functions, respectively:

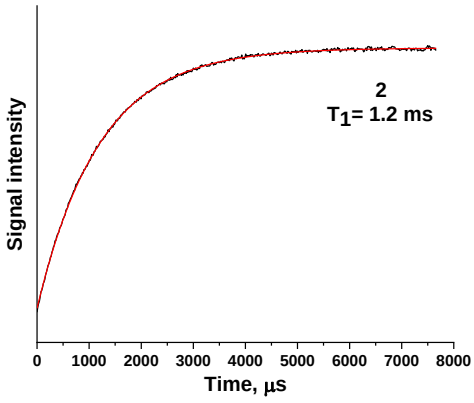
$$I = I_0(1 - \exp(-\frac{\tau}{T_1}))$$

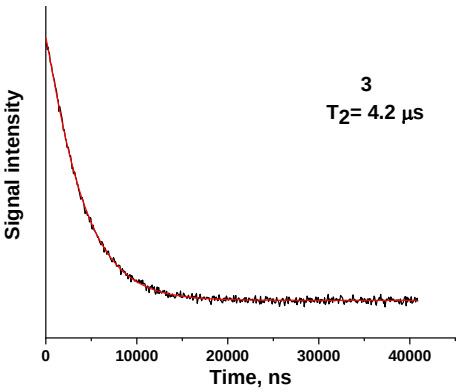
$$I = I_0\exp(-(\frac{\tau}{T_2})^x)$$

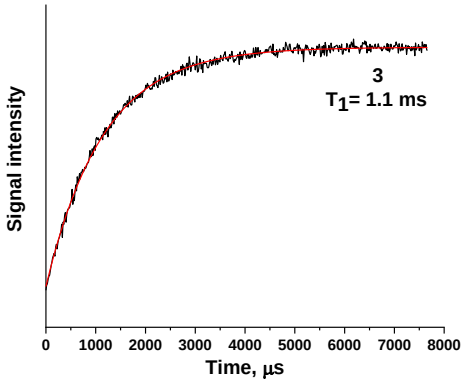












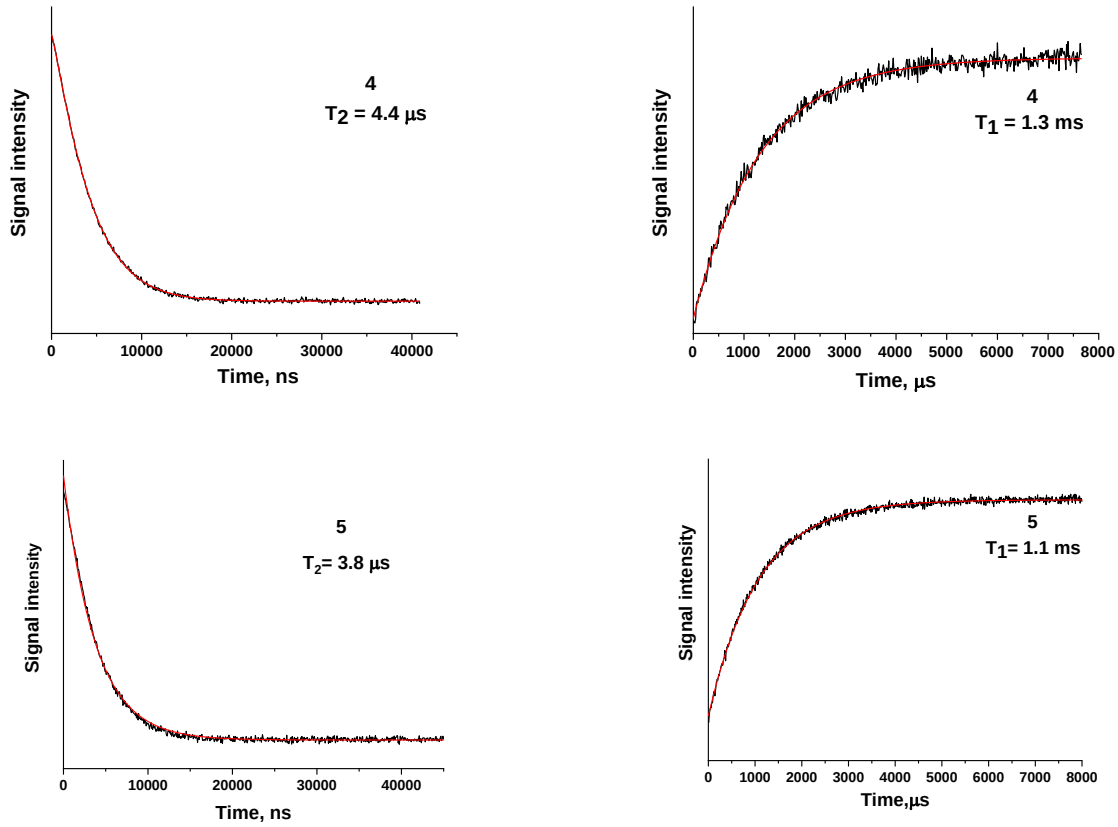


Figure S3. Inversion-recovery time and echo decay traces of **1–5** (black) at 80 K along with mono-exponential fits (red).

Table S2. T_1 and T_2 for compounds **1–5**

Sample	T_1, ms	T_2, µs
Finland trityl	1.7	5.4
1	1.2	4.7
2	1.2	4.4
3	1.1	4.2
4	1.3	4.4
5	1.1	3.8

Optimizing the ENDOR efficiency

For the Mims ENDOR sequence that was used, the dependence of efficiency [as stated in the article by G. Jescke at al[1]. and earlier] of the ENDOR signal on the value of the hyperfine interaction (A) and on τ is known:

$$F = \frac{1}{4}(1 - \cos(A\tau)).$$

In the case of the Pake doublet, the spectra show characteristic splittings equal to $-T$ and $-2T$. We selected the optimum τ for $A = 2T$. Nevertheless, also changing the value of τ allowed us to determine T quite unambiguously. Of course, for small values of T, we must use larger τ, but we are limited by T_2.

Optimizing the RF pulse length

The position of the first maximum is well resolved at 17 μs.

In experiments on compound 5, increasing the RF pulse length did not improve resolution in ENDOR spectra (Fig. S4, right).

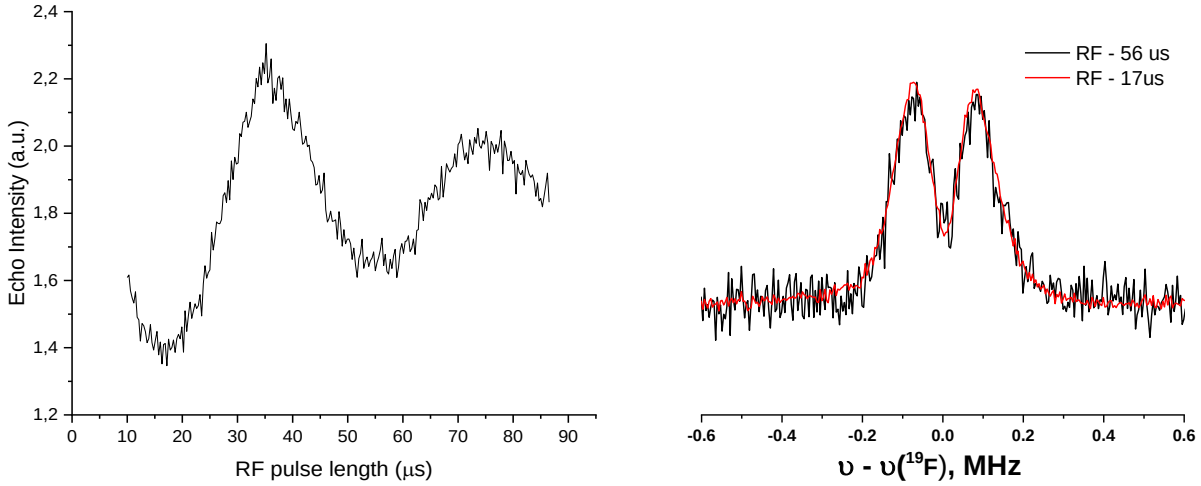


Figure S4. (left) Nuclear spin Rabi oscillations recorded for the ^{19}F resonances on compound **5.** (right) Mims ENDOR of **5** at 80 K and τ = 900 ns at two durations of RF pulses: 17 and 56 μs

Mims ENDOR spectra simulation for compounds 1 and 5

Table S3. *T*⊥ values and calculated distances for compound **1**

τ, ns	*T*⊥, kHz	*T*⊥ *av*, kHz	*r*, Å	*r*$_{av}$, Å
800	122	128 ± 5	8.48	8.3 ± 0.1
2100	130		8.30	
3600	132		8.26	

Table S4. *T*⊥ values and calculated distances for compound **5** (two sets of values)

τ, ns	*T*⊥, kHz	*T*⊥ *av*, kHz	*r*, Å	*r*$_{av}$, Å
500	122 / 184	115 ± 8 / 218 ± 40	8.48 / 7.40	8.7 ± 0.2 / 7.0 ± 0.4
700	122 / 191		8.48 / 7.30	
900	122 / 190		8.48 / 7.32	
2300	116 / 196		8.63 / 7.24	
2700	113 / 213		8.70 / 7.04	
4000	104 / 280		8.95 / 6.43	
4300	103 / 270		8.97 / 6.51	

Spin labeling of human serum albumin (HSA) with a maleimide derivative of FTAM (HSA-FTAM-mal)

The synthetic procedures for FTAM-labeled HSA-FTAM-mal were adapted from the study by Tormyshev et al. [2]. To increase the labeling yield, HSA was reduced using DTT. The reduction of HSA yielding HSA with free Cys-34 (mercaptalbumin or m-HSA-SH) was

performed according to a published procedure [2,3]. Under these conditions, no intramolecular disulfides (protein S-S bridges) were broken by DTT. Briefly, an HSA solution (125 μL, 0.5 mM) in PBS (15 mM KH_2PO_4, 145 mM NaCl, pH 7.4) was mixed with a fourfold excess of the maleimide derivative of the trityl radical (FTAM) dissolved in 7 μL of DMSO, and the mixture was stirred at 37 °C overnight. Unreacted low-molecular-weight materials were removed by centrifugal filtration using Centricon concentrators with PBS as an eluent. Final samples for EPR spectroscopy were prepared using Centricon concentrators and potassium PBS in D_2O as the eluent. The yield of HSA-FTAM-mal was ~90%. UV-vis data on HSA-FTAM-4 (PBS, pH 7.4): λ_{max} 278 nm, 331 nm, 469 nm.

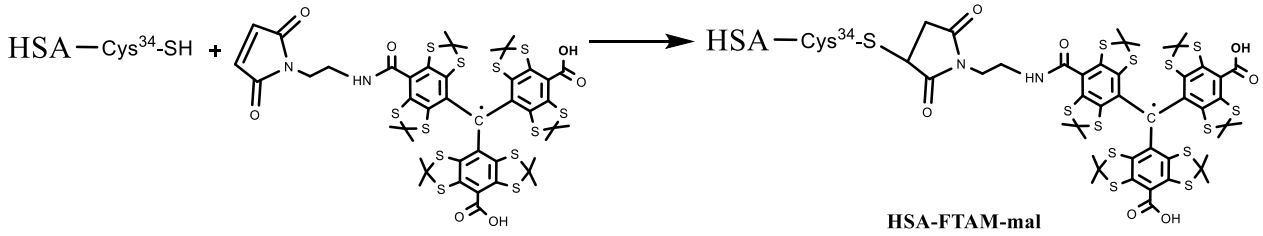


Figure S5. Synthesis of the spin-labeled HSA conjugate by the reaction of the maleimide derivative of the trityl radical with the sulfhydryl group of the Cys-34 albumin side chain.

X-band CW EPR spectra of spin-labeled HSA

CW EPR spectra of spin-labeled HSA in solution were fitted by means of the *EasySpin* package using the *chili* function, which allows for computing a fast, intermediate, and slow rotational tumbling regime of mono-radical species. The spectrum of HSA-MTSL was simulated by two components with correlation times 8.2 (96%) and 0.2 (4%) ns. The spin-Hamiltonian parameters g = [2.0087 2.0057 2.0018] and a_N = [0.60 0.60 3.70] mT were employed.

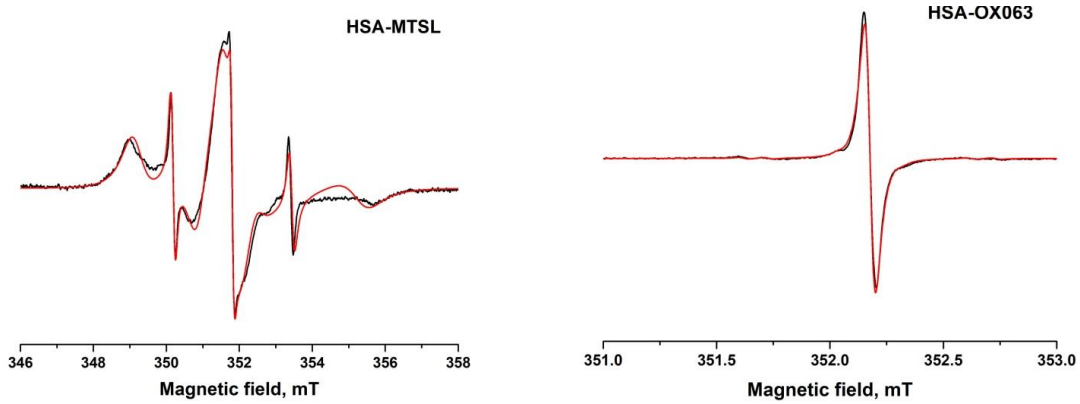


Figure S6. CW spectra of spin-labeled HSA

Relaxation measurements for TAM/MTSL-labeled and fluorinated HSA

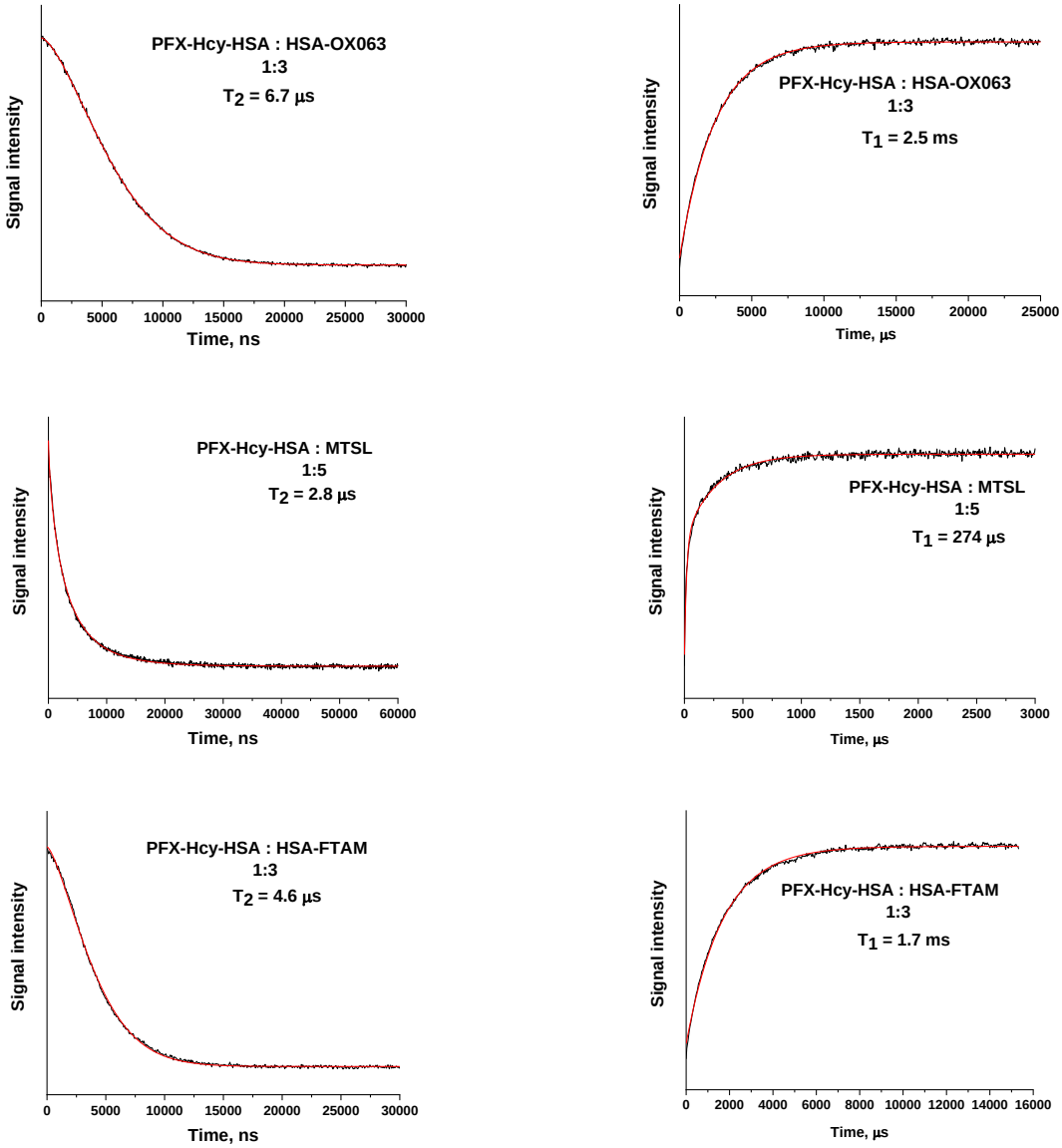


Figure S7. Inversion-recovery time and echo decay traces of TAM/MTSL-labeled and fluorinated HSA (black) at 80 K along with mono-exponential fits (red).

Experimental data on spin-lattice relaxation (T_1) and phase relaxation (T_2) were processed in the same way as for model compounds **1–5**.

Table S5. T_1 and T_2 values for TAM/MTSL-labeled and fluorinated HSA

Sample	T_1, ms	T_2, µs
PFX-Hcy-HSA:MTSL(1:5)	0.3	2.8
PFX-Hcy-HSA:HSA-OX063 (1:3)	2.5	6.7
PFX-Hcy-HSA:HSA-FTAM (1:3)	1.7	4.6

Mims ENDOR for TAM-labeled and fluorinated HSA

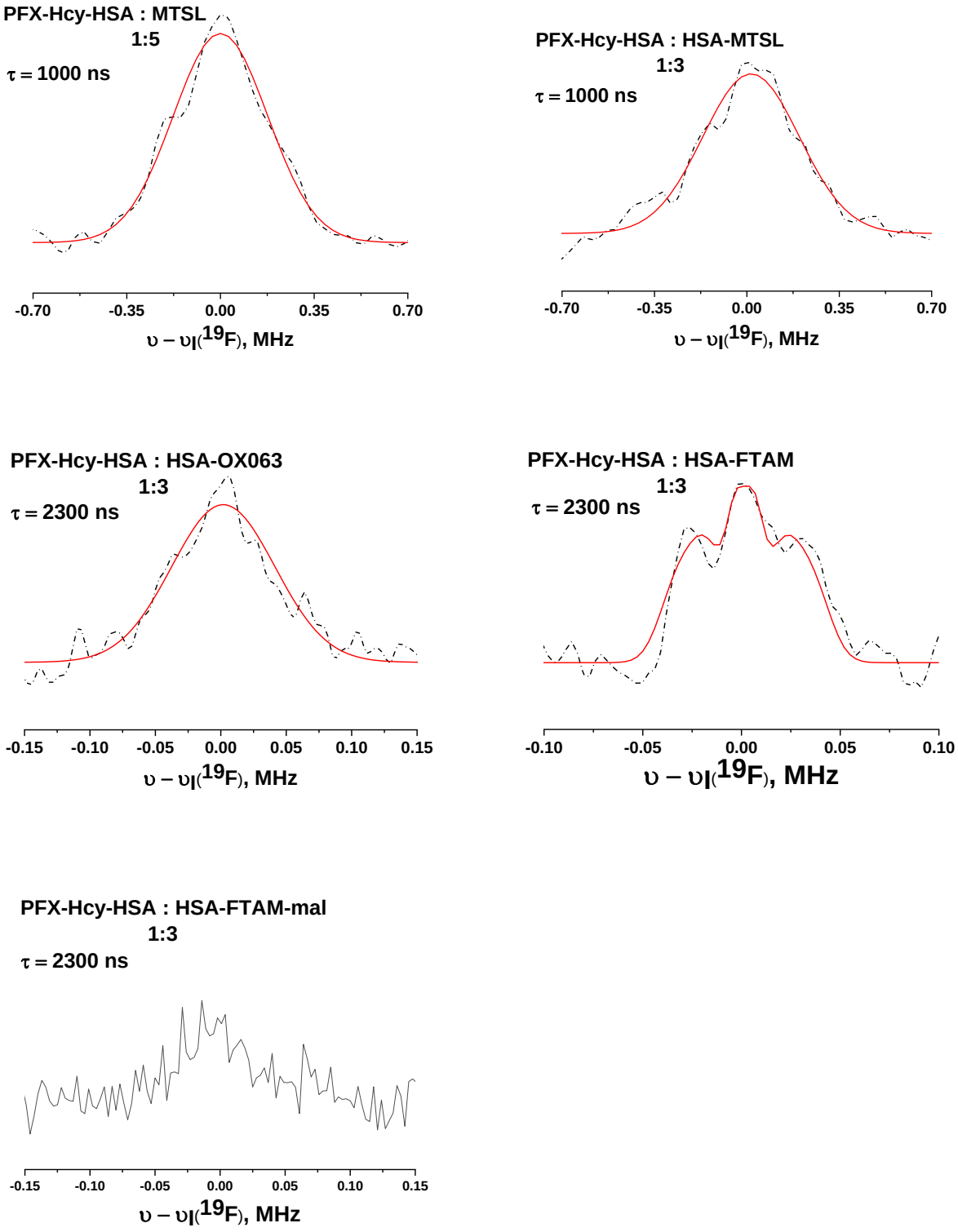


Figure S8. 94 GHz ^{19}F Mims ENDOR spectra of spin-labeled HSA samples in K-PBS-D_2O/ [d_8] glycerol (1:1). Experimental data: black, simulation: red. The relative intensity of the last spectra was ~5 times smaller and in our opinion corresponds to noncovalent dimers of HSA, detected previously using DEER [4] [A. Chubarov, A. Spitsyna, O. Krumkacheva, D. Mitin, D. Suvorov, V. Tormyshev, M. Fedin,

M. K. Bowman and E. Bagryanskaya, *Molecules*, 2021, **26**, 108].

Molecular dynamics (MD) simulations for radical 1

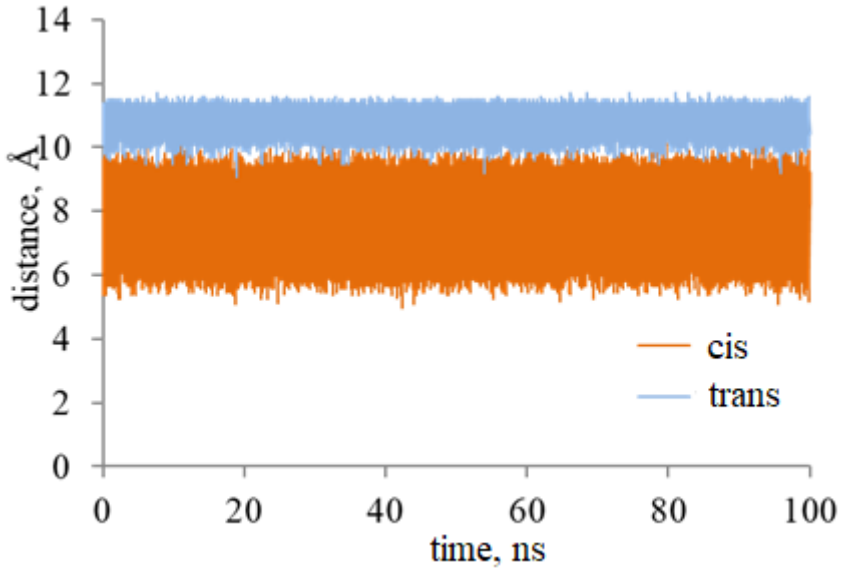


Figure S9. Distances between spin labels and distance distributions for radical **1.**

^{19}F-NMR PRE Measurements

Radical **5**

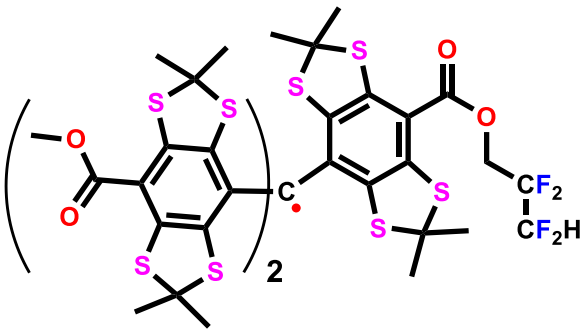


Table S6. Line broadening for radical **5**.

C, mM	Line broadening, Hz	
	-CF_2-	-CF_2H
7.6582	5.942	18.148
3.8291	4.685	27.877
1.9146	5.6870	44.472
0.9573	7.464	62.337
0.4786	10.155	77.155
0.2553	16.31	103.851
0.1197	32.432	186.445

0.0598	66.432	299.367

Radical **1**

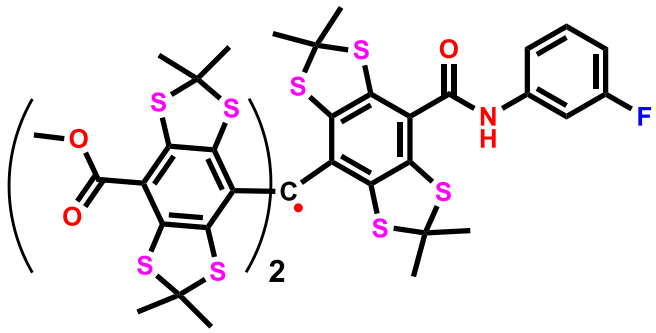
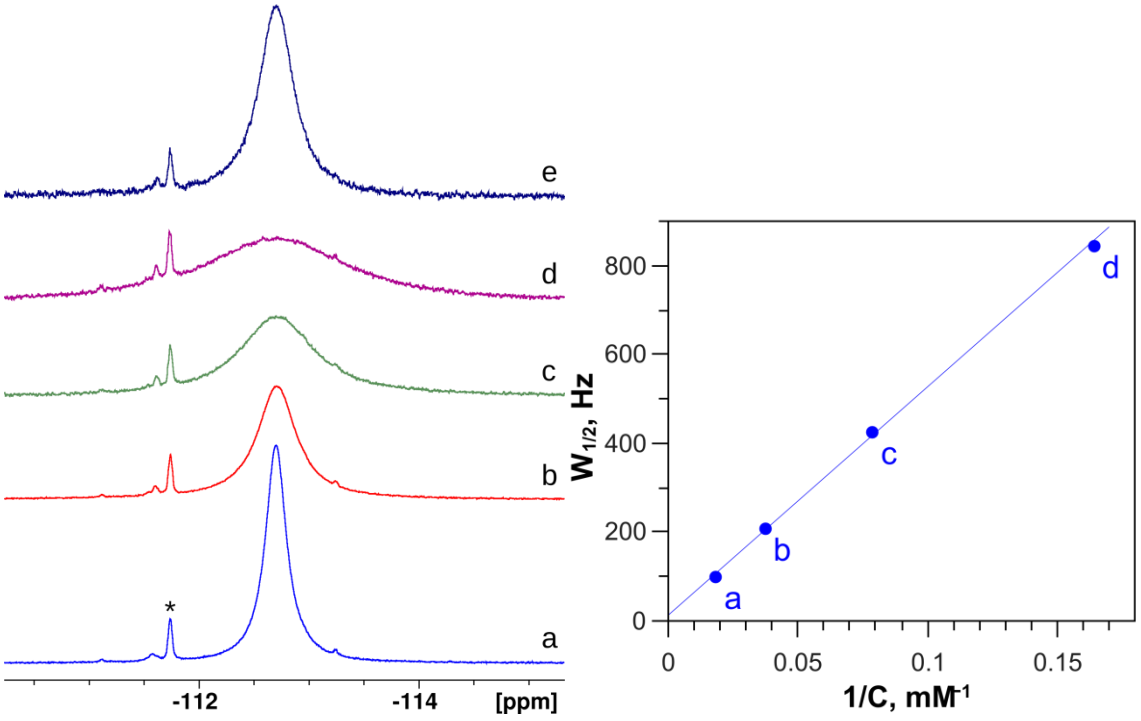


Table S7. Line broadening for radical **1**.

C, mM	Line broadening, Hz
56.39	103.608
26.66	210.852
12.80	427.566
6.10	845



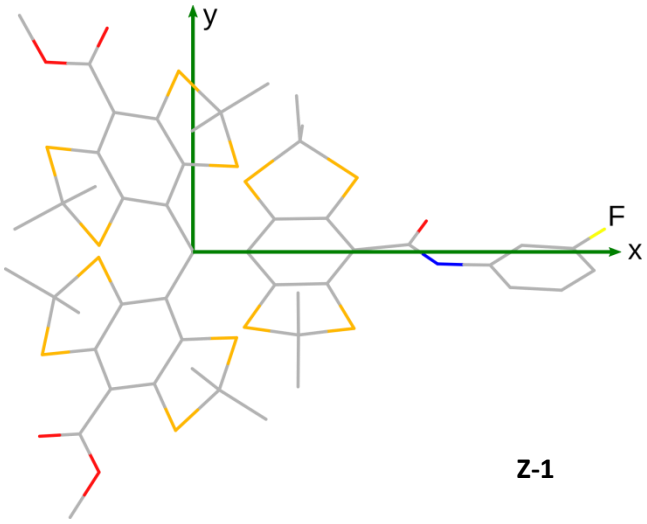
a) **b)**

Figure S10 a) ^{19}F NMR spectra of radical **1** in toluene-d_8 at 27 °C depending on dilution. Before the recording of spectra, the samples were saturated with either argon (a–d) or air (e). Concentrations (mM): 56 (a), 27 (b), 13 (c), or 6.1 (d,e). The asterisk marks the signal of the diamagnetic impurity (m-fluoroaniline). **S10b**. Dependence of broadening of radical **1**'s ^{19}F

NMR signal on the reciprocal of concentration. Intercept: 16 ± 6 Hz and slope: 5100 ± 100 (fitting with statistical weighting, QtiPlot software).

Cartesian coordinates (XMol xyz format) of the stablest conformers of radicals 1–5

Orientation: the origin of coordinates coincides with the radical center; the x-axis passes along the C$^{\bullet}$–Ar bond; the z axis is perpendicular to the plane of the trigonal radical center.



Z-1

z-1

```
114
  Energy -193.966011207580
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 C     2.16584051   0.82223789   0.87483823
 C     3.55605764   0.79434180   0.89471159
 S     4.36724829   1.89611678   1.96819990
 C     2.84213465   2.33195708   2.95309331
 C     1.43708172   0.00000000   0.00000000
 C     2.17172378  -0.82904142  -0.87041043
 C     3.56071897  -0.87188807  -0.83922538
 C     4.28125955  -0.06651472   0.05542866
 S     4.27931488  -1.95375869  -2.02749825
 C     2.80144087  -3.04483925  -2.19805592
 S     1.36069403  -1.89643981  -2.00380186
 C     0.00000000   0.00000000   0.00000000
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 C    -0.25636507  -0.76858848   2.34268280
 C    -0.96100557  -0.78966193   3.53904485
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 C     0.73647957  -2.82985722   3.72536041
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 S    -2.50115627   1.81644053   0.16914009
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 S    -3.89494960   1.88916778   2.78271133
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 O    -2.28778579  -0.63704306   5.96288124
 C    -0.02626056  -4.04618118   3.23356815
 C     1.99305828  -3.19531008   4.49013345
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 C    -4.74790857   3.35379182   0.60281263
 C     5.74554222   0.04099665   0.19873468
 N     6.50990910  -0.94163910  -0.31860018
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C	2.74869460	1.40589818	4.15273830
C	-0.72316524	-0.00365163	-1.23255619
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C	-0.29265786	0.76867017	-2.33590010
S	-2.51324109	-1.81856583	-0.13668097
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S	-0.46893798	1.90766023	-4.75469098
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C	-4.99658140	-2.96085291	-0.43992133
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O	-4.08979079	-0.53785466	-4.90339930
C	-0.02474033	4.07681981	-3.11371720
C	1.93883185	3.23292406	-4.46429204
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O	-3.92402442	0.60102690	5.04831927
O	6.20467533	1.00568130	0.82064034
H	-5.71186044	-3.47574479	-1.07677235
H	-4.82489243	-3.55336499	0.45599116
H	-5.41531502	-1.99978649	-0.15092861
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H	-2.84463977	-4.68400134	-0.72585631
H	-3.73068753	-4.62391765	-2.26115122
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H	-0.90344900	3.76609475	-2.55064155
H	0.63815612	4.62693329	-2.44893464
H	1.66283557	3.86417818	-5.30537565
H	2.63657753	3.77221287	-3.82757080
H	2.42719620	2.33755810	-4.84095182
H	2.66071028	-3.77541348	3.85756100
H	2.51140667	-2.29910206	4.82202084
H	1.72625975	-3.78602412	5.36290089
H	0.61058708	-4.65287297	2.59393564
H	-0.35040344	-4.64056960	4.08474003
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H	-1.68418720	3.72201445	2.18745036
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H	2.68919245	0.36896325	3.82441010
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H	3.67647401	-4.29130657	-3.70430994
H	1.90559012	-4.29393571	-3.68998904
H	2.78152061	-2.90580698	-4.34668593
H	2.77288559	-3.57091174	-0.10799897
H	1.91170857	-4.69499377	-1.16582651
H	3.68362533	-4.68978116	-1.13978854
C	-4.62268665	0.59523016	6.29278366
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E-1

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C	7.74919391	0.71957971	0.84840841
C	8.20762377	1.78479652	-0.11309546
H	8.03611022	0.96586409	1.87312681
H	8.15322302	-0.25569007	0.56159600
H	-2.97429265	-1.62264465	7.61644625
H	-3.55291544	0.06584192	7.41926642
H	-4.47502675	-1.26986435	6.69526198
H	-5.27488042	-1.41669230	-6.29424249
H	-4.68650326	0.22234228	-6.73258873
H	-3.72858429	-1.20551640	-7.18254397
C	9.25287273	1.55167713	-0.99807657
C	9.65513833	2.53868674	-1.87762773
C	8.99870132	3.76018978	-1.87643421
C	7.95318788	4.01310206	-1.00774603
C	7.56794137	3.01643906	-0.12508453
H	9.75214424	0.59595326	-1.00488296
H	10.46247271	2.37974276	-2.57248541
O	9.48813469	4.69633784	-2.82621824

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 C    8.95503335   5.88231984  -2.93599287
 F    9.58636369   6.56061568  -3.89510605
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 F    9.03214540   6.64600180  -1.82508962
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4

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133
  Energy -231.171784081127
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 C    2.16388340   0.82732095   0.87581432
 C    3.54872814   0.92927487   0.80357863
 S    4.27759155   2.12846875   1.85266066
 C    2.73628892   3.12244726   2.06537318
 C    1.43338220   0.00000000   0.00000000
 C    2.16888911  -0.73297997  -0.95154955
 C    3.55054803  -0.63358360  -1.01411943
 C    4.26770434   0.16687501  -0.12074256
 S    4.36768601  -1.51352932  -2.28431516
 C    2.98811003  -2.74104723  -2.49569622
 S    1.42823558  -1.82080138  -2.10832628
 C    0.00000000   0.00000000   0.00000000
 C   -0.74554518  -0.02156950   1.21685391
 C   -0.33236846  -0.79176247   2.32701595
 C   -1.14465962  -0.91965142   3.44588046
 C   -2.35596714  -0.22008410   3.54382916
 C   -2.76428201   0.58065840   2.46707309
 C   -1.97289305   0.67388250   1.33369989
 S   -0.63369829  -1.99141562   4.71314840
 C    0.60760399  -2.89512910   3.65106801
 S    1.16273576  -1.69227687   2.36440409
 S   -2.48619725   1.83876188   0.12589052
 C   -4.23876588   1.94897336   0.69593906
 S   -4.23443559   1.51031043   2.50245959
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 C   -4.74946012   3.36462404   0.51415547
 C   -5.06687965   0.92410404  -0.05757773
 C    5.72435324   0.24168734  -0.36585881
 N    6.57693701   0.36321888   0.66521602
 C    3.15756500  -3.87338939  -1.50050447
 C    2.95392726  -3.22271989  -3.93181972
 C    2.57418245   4.07279862   0.89412312
 C    2.77706090   3.83780641   3.40042806
 C   -0.68590675  -0.02083685  -1.26754199
 C   -1.80375234  -0.84878757  -1.48452813
 C   -2.45640031  -0.88403935  -2.70937448
 C   -2.02295585  -0.06522940  -3.76106141
 C   -0.89219297   0.74185160  -3.57150499
 C   -0.24650489   0.77283241  -2.34308734
 S   -2.44198955  -1.90168454  -0.23482919
 C   -3.35383442  -3.02013557  -1.39187495
 S   -3.80142931  -1.97878652  -2.86331578
 S   -0.29396192   1.75800105  -4.84662023
 C    1.29384709   2.21840979  -3.97896419
 S    1.02163804   1.96994695  -2.17490504
 C   -4.61487683  -3.53435242  -0.72718226
 C   -2.42732563  -4.13390730  -1.84204486
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H	-5.25397140	-2.70686612	-0.42933553
H	-1.52803610	-3.71826549	-2.29469559
H	-2.13943307	-4.74249855	-0.98774764
H	-2.93350027	-4.75870504	-2.57409294
H	1.71954917	3.82295127	-5.32758281
H	0.82418651	4.31544988	-3.88319028
H	2.55255626	3.94458439	-3.76836900
H	2.54141401	1.37708091	-5.50931032
H	3.32297934	1.49570888	-3.92064575
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C	-4.93559154	0.40069915	6.06387296
C	-4.53769974	-0.65553273	-6.35740714
C	6.33536125	0.10198559	2.02322807
H	-4.52687697	0.35928410	-6.75795078
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H	-5.54691634	-0.97320588	-6.11103331
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H	7.53574679	0.56141936	0.40143787
C	7.03870483	0.81639662	2.99372964
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H	7.31066655	1.19136101	5.06852520
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C	0.97897925	-0.25031533	7.65041656
C	0.62269031	0.58087269	6.60124773
C	1.49363921	0.83489347	5.56132843
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O	-0.69335625	1.12876229	6.67374661
H	1.20976454	1.45822845	4.72765871
H	3.42183386	0.45689672	4.76173323
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F	-2.19795720	2.63781772	6.39187766
F	-1.06553990	2.07379789	4.66659774
F	-0.14338994	3.23948676	6.19963898
H	4.44217597	-2.19890727	6.13863217
H	4.77013658	-1.44435645	7.69577097

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S	-1.65590784	1.02403958	-2.01127042
C	-0.37487414	1.57527322	-0.95073698
C	-0.04178094	2.91836692	-1.05101133
S	-1.01824802	3.91256585	-2.09008108
C	-2.39835022	2.68822615	-2.29715904
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S	-0.69713795	-3.14344171	-1.77939078
C	-2.00718055	-3.87355017	-2.86119222
S	-3.54546934	-3.95594520	-1.82301844
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O	-6.29757877	-1.65896948	0.68187319
C	-3.08644451	0.07767879	3.99147374
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C	-2.25450200	-2.94912107	-4.03849471
C	-1.60295874	-5.27186968	-3.28302214
C	1.48330804	4.79867040	-0.39110709
O	0.78562218	5.57476497	-1.25168115
C	4.32402432	1.48645727	3.27011916
C	4.86426497	0.97424733	0.85550420
C	-2.95246003	2.77494370	-3.70498622
C	-3.44585456	2.94994906	-1.23099603
C	1.01461581	-1.71736988	0.07285741
C	0.86316586	-2.79029022	0.97385340
C	1.85047193	-3.75959656	1.10158731
C	2.98355275	-3.73647072	0.27760489
C	3.12834566	-2.69949614	-0.65284366
C	2.17779538	-1.68865980	-0.72158598
S	-0.51894041	-2.95252365	2.03219179
C	0.26350722	-4.13924287	3.21083161
S	1.64043939	-5.00221519	2.29590196
S	4.46772656	-2.60722674	-1.75902723

C	3.65760332	-1.39950126	-2.91421146
S	2.48869953	-0.41062299	-1.87787796
C	-0.76380217	-5.16223103	3.65468521
C	0.85883281	-3.36334249	4.37179420
C	3.94892402	-4.81012224	0.44752848
O	3.74399564	-5.76954494	1.17845116
C	2.86560004	-2.16729596	-3.95551769
C	4.70576584	-0.48944365	-3.52113768
O	5.07071763	-4.65163636	-0.24782953
O	-5.76565850	-3.46679767	-0.54033223
O	2.38845439	5.25993848	0.29270352
H	-0.29186092	-5.88746452	4.31315967
H	-1.57441201	-4.67152880	4.18886985
H	-1.17516305	-5.68542971	2.79467168
H	1.56424840	-2.61768429	4.00887628
H	0.07093440	-2.85844265	4.92648394
H	1.38247513	-4.04691554	5.03621709
H	3.53165102	-2.81645032	-4.51930244
H	2.09997459	-2.77698373	-3.47706120
H	2.38169132	-1.47082311	-4.63669675
H	5.39898342	-1.07831801	-4.11635736
H	4.22781251	0.25022866	-4.15925940
H	5.26247794	0.02451855	-2.74172172
H	-3.16757370	2.83853618	3.63552203
H	-4.20944238	2.82930894	2.20543186
H	-4.82159368	2.21200392	3.74331245
H	-2.31577805	0.58867790	4.56501125
H	-3.96719524	-0.05745746	4.61525529
H	-2.71210455	-0.90153237	3.69539033
H	-0.69523025	-5.23035453	-3.88029590
H	-1.42169701	-5.89563773	-2.41094168
H	-2.39792485	-5.71794036	-3.87534637
H	-1.35860040	-2.88466661	-4.65150601
H	-3.07394964	-3.33440777	-4.64075749
H	-2.51094876	-1.94960985	-3.69096754
H	-3.34160490	3.77468356	-3.88086669
H	-2.17346874	2.56584765	-4.43345141
H	-3.75732624	2.05448177	-3.82952902
H	-3.00280059	2.88326724	-0.23809968
H	-3.86181680	3.94665799	-1.35998623
H	-4.24586346	2.21550027	-1.30448060
H	5.69427978	1.67662433	0.85629253
H	5.22918573	-0.01382003	1.12851953
H	4.44529273	0.92767591	-0.14818602
H	3.53696067	1.80830768	3.94741757
H	4.67425786	0.50367002	3.57717871
H	5.14853672	2.19247451	3.32987311
C	-7.13198569	-3.87996000	-0.52545114
C	6.05633713	-5.67822208	-0.13604739
C	1.14819721	6.93498784	-1.32703008
H	6.88820140	-5.35096811	-0.75227557
H	6.35873510	-5.79168569	0.90632107
H	5.65070311	-6.62600666	-0.49360906
H	-7.15627697	-4.82456579	-1.06032659
H	-7.47309472	-4.00148034	0.50394427
H	-7.75333098	-3.13197388	-1.02047738
C	0.42508589	7.80260628	-0.28636448
H	2.22661515	7.05275683	-1.16703134
H	0.85569593	7.27979003	-2.32128642
C	0.50026460	7.28720150	1.16867848
F	0.97982554	9.04532597	-0.30772131
F	-0.87632029	7.98550875	-0.62938329
H	1.53659129	7.11092924	1.48980237
F	-0.07447049	8.18399134	1.99833921

F -0.20609741 6.14343749 1.29750517

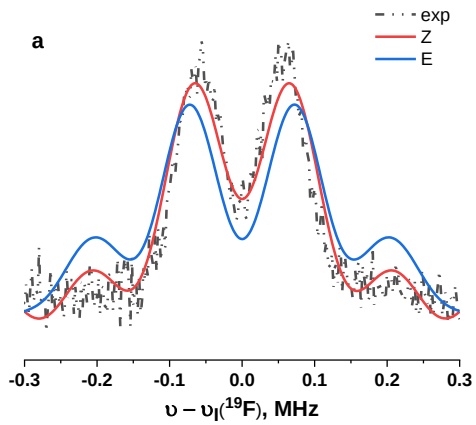
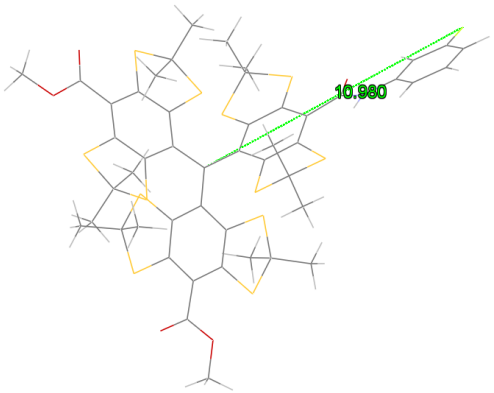
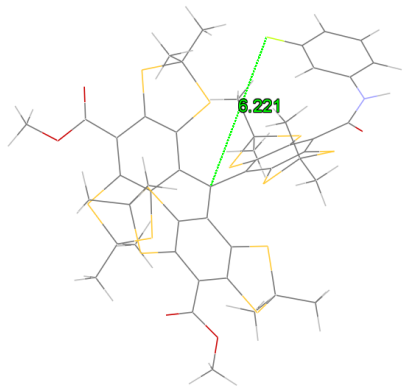
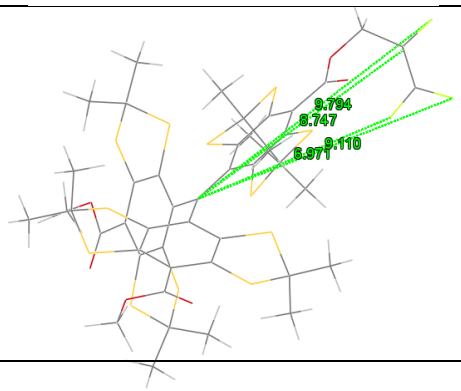
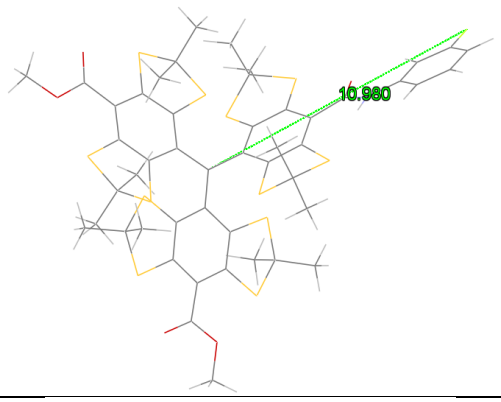
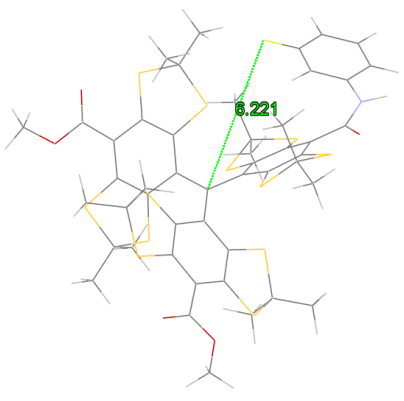


Figure S11. Experimental and simulated Mims ENDOR spectra (EasySpin) taking into account anisotropic hfi calculated using ORCA. Structures and hfi tensors are shown below in Table 8.

Table S8. Structures and corresponding calculated *hfi* tensors.

Method	Structure	HFI tensors, MHz
1 Z UKS TPSSh def2-tzvp TightSCF		0.1996 0.0640 0.0556 0.0640 -0.1608 0.3698 0.0556 0.3698 -0.6660 A(FC) -0.2091 -0.2091 -0.2091 A(SD) 0.2094 0.4431 -0.6525 A(Tot) 0.0003 0.2341 -0.8616 A(iso)= -0.2091
1 E UKS TPSSh def2-tzvp TightSCF		-0.1335 0.3029 0.1102 0.3029 0.1225 -0.2350 0.1102 -0.2350 -0.4558 A(FC) -0.1556 -0.1556 -0.1556 A(SD) -0.0223 0.5039 -0.4816 A(Tot) -0.1779 0.3483 -0.6372 A(iso)= -0.1556
5 UKS TPSSh def2-tzvp TightSCF		-CF_2- 107F (9.8 Å) -0.0892 -0.1010 -0.0413 -0.1010 0.6094 0.2278 -0.0413 0.2278 0.0439 A(FC) 0.1881 0.1881 0.1881 A(SD) -0.2241 -0.2926 0.5167 A(Tot) -0.0361 -0.1045 0.7047 A(iso)= 0.1881

		108F (9.8 Å) -0.0244 -0.1566 -0.1865 -0.1566 0.1752 -0.0048 -0.1865 -0.0048 -0.0024 A(FC) 0.0495 0.0495 0.0495 A(SD) 0.0416 -0.2854 0.2438 A(Tot) 0.0911 -0.2360 0.2933 A(iso)= 0.0495
		$-CHF_2$ 110F(9.1 Å) -0.0229 -0.1725 0.0472 -0.1725 0.3117 0.0575 0.0472 0.0575 -0.1022 A(FC) 0.0622 0.0622 0.0622 A(SD) -0.0966 -0.2284 0.3250 A(Tot) -0.0344 -0.1661 0.3872 A(iso)= 0.0622 111F(7.0 Å) -0.2714 -0.1793 -0.0687 -0.1793 0.6497 0.1398 -0.0687 0.1398 -0.2787 A(FC) 0.0332 0.0332 0.0332 A(SD) -0.2953 -0.3778 0.6731 A(Tot) -0.2621 -0.3446 0.7063 A(iso)= 0.0332
AMG 1 Z UKS B3LYP IGLO-II TightSCF		0.1871 0.0518 0.0415 0.0518 -0.1479 0.3010 0.0415 0.3010 -0.5624 A(FC) -0.1744 -0.1744 -0.1744 A(SD) 0.1633 0.3830 -0.5464 A(Tot) -0.0111 0.2086 -0.7208 A(iso)= -0.1744
AMG 1 E UKS B3LYP IGLO-II TightSCF		-0.1239 0.3042 0.0646 0.3042 0.1228 -0.2340 0.0646 -0.2340 -0.4254 A(FC) -0.1422 -0.1422 -0.1422 A(SD) -0.0606 0.5037 -0.4431 A(Tot) -0.2028 0.3616 -0.5852 A(iso)= -0.1422

Applicability of the point dipole approximation to distance measurement in the TAM–fluorine pair

Dipole–dipole interaction of electron and nuclear spins is proportional to the inverse cube of distance between them, and therefore measurements of the spectroscopic manifestations of this interaction provide useful information on the system structure. Estimation of the interspin distance by radiospectroscopic techniques is a direct method of structural analysis. There is a problem, however, due to electron spin density distribution in bulky radicals such as a trityl radical. The nuclear spin is definitely a point object, whereas the electron spin is not. Thus, the question about distance between the two spins is not so trivial; we know well where vector, $\boldsymbol{r}_{IS}$, connecting nuclear spin $\boldsymbol{I}$ and electron spin $\boldsymbol{S}$, starts, but it is unclear where exactly it ends and which atom of a radical it points to, even in the case when its length is estimated from experiment [5,6][C. Riplinger, J. P. Y. Kao, G. M. Rosen, V. Kathirvelu, G. R. Eaton, S. S. Eaton, A. Kutateladze and F. Neese, *J. Am. Chem. Soc.*, 2009, **131**, 10092–10106, S. Stoll and R. D. Britt, *Phys. Chem. Chem. Phys.*, 2009, **11**, 6614–6625]. Quantum mechanical calculations may help in this case, but when there are many conformations of a molecule in question, such calculations become time consuming. It should be noted that each molecular conformation possesses its own spin Hamiltonian of dipole–dipole interaction, and therefore the ENDOR spectrum will be a weighted sum of spectra originating from each conformation, and the weight is the conformation population proportional to the respective Boltzmann factor in the case of a thermal equilibrium.

Here we will ignore isotropic hyperfine interaction (HFI) by considering only its anisotropic dipole–dipole part.

Dipole interaction is described with a tensor, **D**, so that its spin Hamiltonian is

$$\hat{H} = \hat{\boldsymbol{S}}\boldsymbol{D}\hat{\boldsymbol{I}} \tag{1}$$

The cap over a symbol means a quantum mechanical operator. Tensor **D** is traceless if isotropic HFI is ignored. The nuclear spin is well localized in a molecule and is regarded as a point object. The electron spin is distributed in a space with a spin density of $\rho(\boldsymbol{r})$. Tensor **D** may be calculated as

$$\boldsymbol{D} = A\int \rho(\boldsymbol{r})dV\left(\frac{\mathbf{1}-3\boldsymbol{n}_{IS}\otimes\boldsymbol{n}_{IS}}{r_{IS}^3}\right) \tag{2}$$

Here A is a constant, operator $\otimes$ means the outer product of the two vectors, $\boldsymbol{n}_{IS} = \boldsymbol{r}_{IS}/r_{IS}$, and spin Hamiltonian (1) takes the form of

$$\widehat{H} = A \int \rho(\boldsymbol{r}) dV \frac{\widehat{\boldsymbol{S}}\widehat{\boldsymbol{I}} - 3(\boldsymbol{n}_{IS}\widehat{\boldsymbol{I}})(\boldsymbol{n}_{IS}\widehat{\boldsymbol{S}})}{r_{IS}^3} \quad (1`)$$

Cartesian components of tensor (2) may be written as [7]

$$D_{ij} = A \int \rho(\boldsymbol{r}) dV \left(\frac{\delta_{ij} - 3n_i n_j}{r_{IS}^3} \right) \quad (3)$$

where *i* and *j* denote axes of some frame used for tensor components' calculations.

We are interested in energy level corrections caused by spin Hamiltonian (1) in the case of weak spin–spin coupling because measurements were performed with the help of a W-band EPR spectrometer (magnetic field of 3.5 T), and therefore Zeeman frequency of the ^{19}F nucleus is ~140 MHz. In high magnetic fields, the radical spin Hamiltonian may be solved by choosing quantization axes for electron and nuclear spins along the external field direction, and dipole energy corrections may be calculated by collecting only those terms in Eq. (1) that contain product $\hat{S}_z\hat{I}_z$, where the *z*-axis is directed along the external magnetic field, which is also the *z*-axis of the lab frame. These corrections provide level shifts in the first order of perturbations. The above reasoning may be rephrased as follows: the secular part, $\widehat{H}_{sec}$, of dipole interaction (1) is

$$\widehat{H}_{sec} = \hat{S}_{\boldsymbol{z}} D_{\boldsymbol{zz}} \hat{I}_{\boldsymbol{z}} \quad (4)$$

Finally, we need to estimate the only tensor $\boldsymbol{D}$ component in the lab frame, $D_{\boldsymbol{zz}}$.

The spherically symmetric case

In the case of spherically symmetric spin density distribution $\rho(\boldsymbol{r}) = \rho(r)$, spin density depends on the distance from the molecular frame origin and does not depend on the direction of vector $\boldsymbol{r}$. The molecular frame may be specified by choosing the position of the fluorine nucleus at the point having coordinates $\boldsymbol{r_I} = (0, 0, r_I)$, thus defining molecular axis Z. The distance between the center of the electron spin density distribution and the nucleus is r_I. In this frame, tensor $\boldsymbol{D}$ is diagonal and possesses axial symmetry, its general property is traceless, and its principal values are

$$D_{\mathrm{XX}} = D_{\mathrm{YY}} = D_{\perp} = A/r_I^3 \quad (5)$$

$$D_{\mathrm{ZZ}} = D_{\parallel} = -2D_{\perp} = -2A/r_I^3 \quad (6)$$

In the case of spherical symmetry of the spin density distribution, dipole coupling of the nuclear spin is proportional to the inverse cube of the distance between the center of the electron spin density distribution and the position of a nucleus in a radical. The first-order energy correction is proportional to $D_{\boldsymbol{zz}}$, see Eq. (4); this quantity may be calculated using relations (5,6) and

presented as $D_{zz} = \boldsymbol{b}.\boldsymbol{D}.\boldsymbol{b}$, where $\boldsymbol{b} = (sin\Theta\, cos\Phi, sin\Theta\, sin\Phi, cos\Theta)$ is a unit vector along the external field direction (z-axis of the lab frame), angles Θ and Φ specify the direction of this field in the molecular frame, its symmetry axis is directed along vector $\boldsymbol{r_I}$, and therefore Θ is the angle between this vector and the external field. Finally, as expected,

$$D_{zz} = A\,(1 - 3cos^2\Theta)/r_I^3 \tag{7}$$

A realistic spin density distribution in TAM radicals

TAM radicals are "round" enough, and it has also been shown that for a family of such radicals with different side substituent groups, isotropic HFI constants of ^{13}C nuclei in the core part of a molecule are pretty stable; they do not depend either on a substituent group's structure or on the solvent in which the radicals are dissolved [8] [G. Fanali, A. di Masi, V. Trezza, M. Marino, M. Fasano and P. Ascenzi, *Mol. Aspects Med.*, 2012, **33**, 209–290]. This means that it is reasonable to perform numerical calculations of tensor $\boldsymbol{D}$ taking into account the spin density distribution as a sum of delta-functions centered at carbon and sulfur atoms of the core part of the TAM radical because we are interested in distances much greater than the sizes of molecular orbits where an unpaired electron is distributed, the weight of each point can be assumed to be the sum of spin densities of the unpaired electron in the s- and p-orbits provided by quantum chemical calculations, for E conformation for definiteness (details are provided in SI). In such a model, spin density is distributed at a central carbon atom (~60%) and at the other conjugated carbon atoms (seven atoms in each of three rings) and at all 12 sulfur atoms; therefore, the number of centers of spin density localization, n_C, is 34. Positions of all the needed carbon and sulfur nuclei are taken from the list of coordinates for the E conformation of the radical presented in SI. Accordingly, the spin density distribution in this approximation may be written as

$$\rho(\boldsymbol{r})dV = \left(\sum_{i=1}^{n_C} w_i \delta(x - x_i)\delta(y - y_i)\delta(z - z_i)\right)dxdydz \tag{8}$$

Here vector $(x_i, y_i, z_i) = \boldsymbol{R}_i$ denotes coordinates of the *i*th atom taken from the table mentioned above, and for our estimates, we apply the formula

$$w_i = \left(\rho_{is} + \rho_{ip}\right)/N \tag{9}$$

where ρ_{is} and ρ_{ip} are respectively spin densities in s and p orbits at the *i*th atom possessing spin density, and $N = \sum\left(\rho_{is} + \rho_{ip}\right)$ is a normalizing factor. Alternation of spin density signs on the trityl carbon atoms is shown by quantum mechanical calculations and is taken into account explicitly. Let us calculate tensor $\boldsymbol{D}$ for an arbitrary position of a nucleus in the space given by vector $\boldsymbol{r_I}$, counting from the central carbon atom; for the calculations, we will employ the frame

where conformational data are presented in SI, and compare the results with those for the spherically symmetric spin density distribution given by Eqs. (5,6).

Explicit equations for the tensor components (constant A is omitted for simplicity) in the frame specified are

$$D_{xx} = D_0 - 3\sum_{i=1}^{n_C} w_i \left(x_i - r_{I,x}\right)^2 / |\boldsymbol{R}_i - \boldsymbol{r_I}|^5 \quad (10.1)$$

$$D_{xy} = D_{yx} = -3\sum_{i=1}^{n_C} w_i \left(x_i - r_{I,x}\right)\left(y_i - r_{I,y}\right) / |\boldsymbol{R}_i - \boldsymbol{r_I}|^5 \quad (10.2)$$

$$D_{yy} = D_0 - 3\sum_{i=1}^{n_C} w_i \left(y_i - r_{I,y}\right)^2 / |\boldsymbol{R}_i - \boldsymbol{r_I}|^5 \quad (10.3)$$

$$D_{xz} = D_{zx} = -3\sum_{i=1}^{n_C} w_i \left(x_i - r_{I,x}\right)\left(z_i - r_{I,z}\right) / |\boldsymbol{R}_i - \boldsymbol{r_I}|^5 \quad (10.4)$$

$$D_{yz} = D_{zy} = -3\sum_{i=1}^{n_C} w_i \left(z_i - r_{I,z}\right)\left(y_i - r_{I,y}\right) / |\boldsymbol{R}_i - \boldsymbol{r_I}|^5 \quad (10.5)$$

$$D_{zz} = -D_{xx} - D_{yy} \quad (10.6)$$

$$D_0 = \sum_{i=1}^{n_C} w_i / |\boldsymbol{R}_i - \boldsymbol{r_I}|^3 \quad (10.7)$$

For a distant nucleus, when

$$\max_i |\boldsymbol{R}_i| \ll |\boldsymbol{r_I}| \quad (11)$$

tensor $\boldsymbol{D}$ is diagonal and axial with good accuracy in a frame with the Z axis directed along vector $\boldsymbol{r_I}$. Its principal values are

$$D_{XX} \approx D_0\left(1 + O([\max_i |\boldsymbol{R}_i| / |\boldsymbol{r_I}|]^2)\right) \quad (12.1)$$

$$D_{YY} \approx D_0\left(1 + O([\max_i |\boldsymbol{R}_i| / |\boldsymbol{r_I}|]^2)\right) \quad (12.2)$$

$$D_{ZZ} \approx -2D_0\left(1 + O([\max_i |\boldsymbol{R}_i| / |\boldsymbol{r_I}|]^2)\right) \quad (12.3)$$

$$D_0 \approx A / |\boldsymbol{r_I}|^3 \quad (12.4)$$

Here $O(x)$ means "having a value of the order of *x*." The exact relation for these approximate quantities is $D_{XX} + D_{YY} + D_{ZZ} = 0$. Off-diagonal elements of the tensor are small in this frame,

$$D_{XY} = D_{XY} \propto D_0 O([\max_i |\boldsymbol{R}_i| / |\boldsymbol{r_I}|]^2) \quad (13.1)$$

$$D_{X(Y)Z} = D_{ZX(Y)} \propto D_0 O([\max_i |\boldsymbol{R}_i| / |\boldsymbol{r_I}|]) \quad (13.2)$$

Asymmetry of dipole interaction, *E*, is defined as

$$E = D_{XX} - D_{YY} \quad (14)$$

The dimensionless quantity for characterizing dipole coupling asymmetry, η, is defined as

$$\eta = |(D_{XX} - D_{YY}) / D_{ZZ}| \quad (15)$$

This parameter is in the range $0 \leq \eta \leq 1$. For a distant nucleus, it is small and may be estimated as

$$\eta \approx 1.5\left|\sum_{i=1}^{n_C} w_i \left(Y_i^2 - X_i^2\right)/|\boldsymbol{r_I}|^2\right| \quad (16)$$

For a nonaxial dipole interaction (when $\eta > 0$), each Pake doublet component has three turning points instead of two in an axially symmetric case. The most intensive point, where spectral density approaches infinity, moves to the center of the spectrum thus shifting the distance estimate to larger values. Fortunately, this correction is small for the distant nucleus and becomes significant only when the nucleus in question is close enough to the center of the radical, and spin density distribution is not symmetric in such a case.

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