Supplementary Information:

Structural Control over Spin Localization in Triarylmethyls

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EPR line-widths and calculated dipole-dipole couplings

In ref.[16], the TAM radicals 1-9 (numbers correspond to the labeling used in ref.[16], in our manuscript they are labeled as TAM13-21, correspondingly - see chemical structures below) are in dilute solutions and interactions between molecules are relatively rare and weak and their effect on the unpaired electron state can be neglected for calculation of spin dipolar (i.e. anisotropic dipole-dipole) couplings. This situation justifies our use of isolated molecule calculations. Although anisotropic dipole-dipole interactions are often not observed in solution where there is no a specific molecular orientation, it is known that for slow molecular tumbling rates (like in measurements done at low temperatures and/or with high viscosity solvents) EPR line-widths are proportional to the modulation of the dipole-dipole interactions through molecular tumbling (ref [16]). Since the EPR measurements in ref.[16] were done at low temperature (163K) in $CFCl_3$, except for Rad8 and Rad9 (notation of ref.[16]) which were measured at room temperature in tetrahydrofuran, the line-widths can be reasonably assumed to depend on the dipole-dipole interactions.

Specifically, we use the 3ZZ-RR components of the tensor of only the anisotropic dipole-dipole couplings (i.e. without the isotropic part). The Z component is taken as it is parallel to the p_z orbitals which form the conjugated pi system of TAM molecules, which provides the means for the delocalisation of the unpaired electron.

In Fig. 1 we plot the experimental line-widths (black circles) together with our calculated mean dipole-dipole couplings (red rhombuses) for the radical series of Ref. [16] (note that the mean dipole-dipole couplings are obtained by taking the average of the 3ZZ-RR components over all the atoms of each radical). The excellent agreement between the trends in both data sets, suggest that our calculations are able to capture very small variations of the EPR line-widths, confirms the accuracy of our computational approach. This match, additionally, appears to confirm the existence of a causal link between line-widths and dipole-dipole interactions.

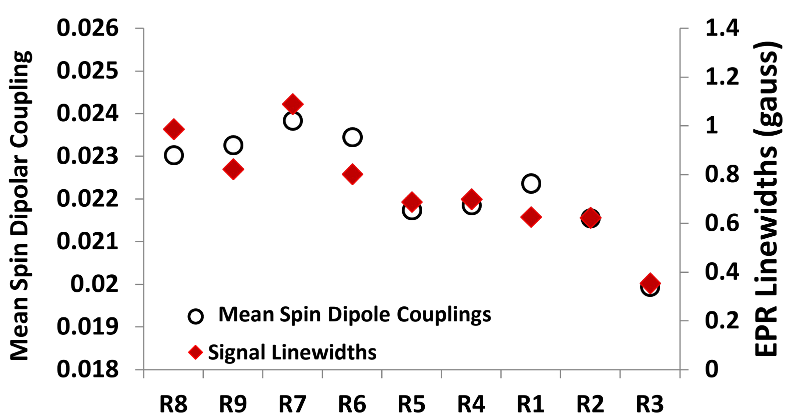

Figure 1. Experimental ESR line-widths (*black circles*) and calculated mean dipole-dipole couplings (*red*) provided by Gaussian09 for all reported radicals in ref.[16].

Chemical Structures of TAMs 1-25

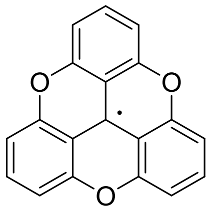

Figure 2. TAM1 chemical structure.

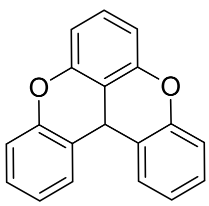

Figure 3. TAM2 chemical structure.

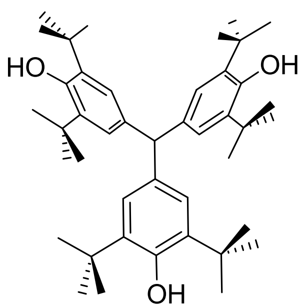

Figure 4. TAM3 chemical structure.

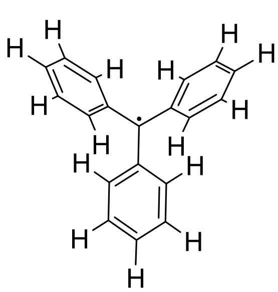

Figure 5. TAM4 chemical structure. This is the triphenylmethyl. First TAM (and organic radical) ever synthesized.

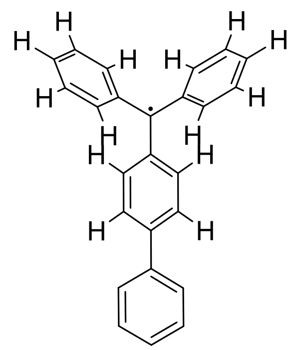

Figure 6. TAM5 chemical structure.

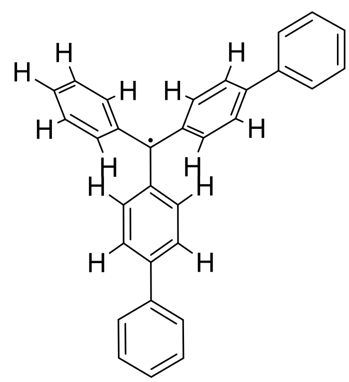

Figure 7. TAM6 chemical structure.

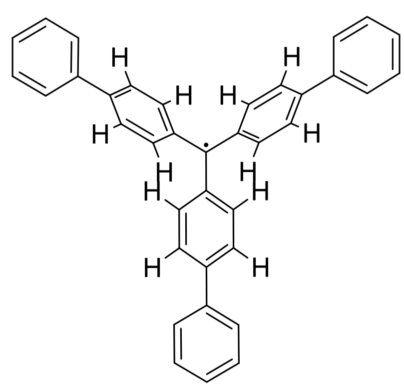

Figure 8. TAM7 chemical structure.

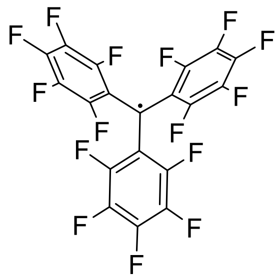

Figure 9. TAM8 chemical structure.

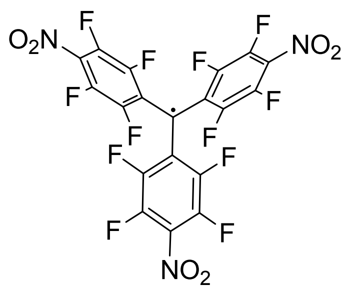

Figure 10. TAM9 chemical structure.

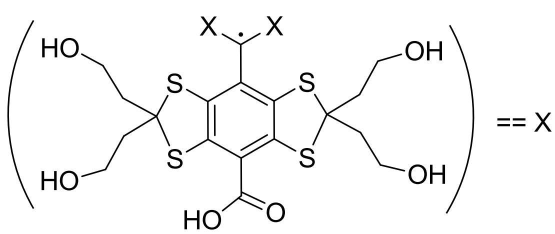

Figure 11. TAM10 chemical structure. This is the so-called OX63, a commercial TAM commonly used in DNP, oxygen detection or spin labeling.

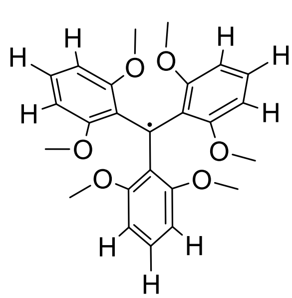

Figure 12. TAM11 chemical structure.

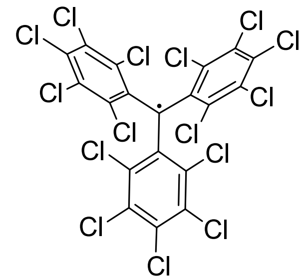

Figure 13. TAM12 chemical structure. This is the polychlorotriphenylmethyl, commonly abbreviated as PTM. Also Rad1 in ref. [16].

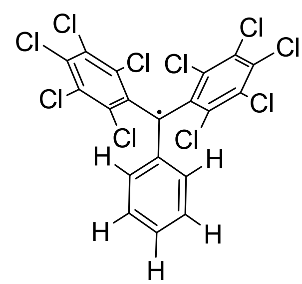

Figure 14. TAM13 chemical structure. Also Rad2 in ref. [16].

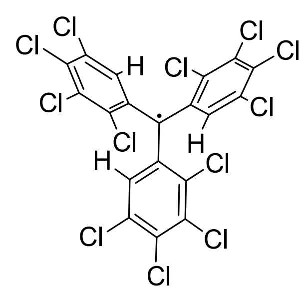

Figure 15. TAM14 chemical structure. Also Rad3 in ref. [16].

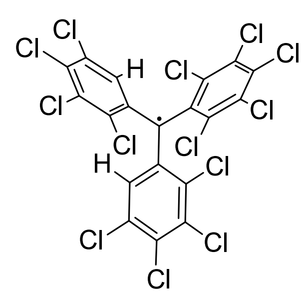

Figure 16. TAM15 chemical structure. Also Rad4 in ref. [16].

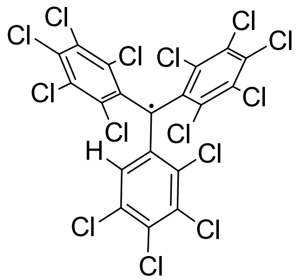

Figure 17. TAM16 chemical structure. Also Rad5 in ref. [16].

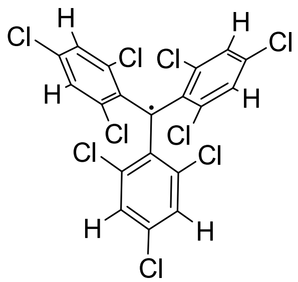

Figure 18. TAM17 chemical structure. Also Rad6 in ref. [16]

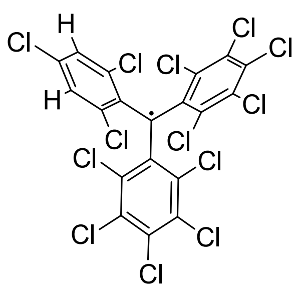

Figure 19. TAM18 chemical structure. Also Rad7 in ref. [16]

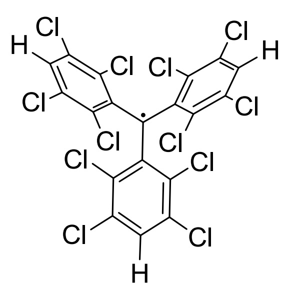

Figure 20. TAM19 chemical structure. Also Rad8 in ref. [16].

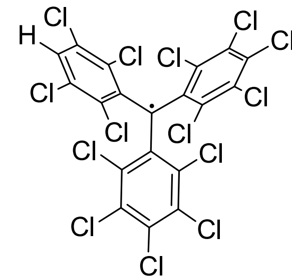

Figure 21. TAM20 chemical structure. Also Rad9 in ref. [16]

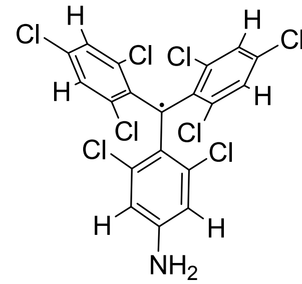

Figure 22. TAM21 chemical structure.

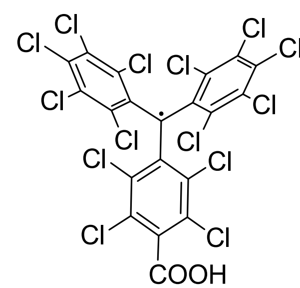

Figure 23. TAM22 chemical structure.

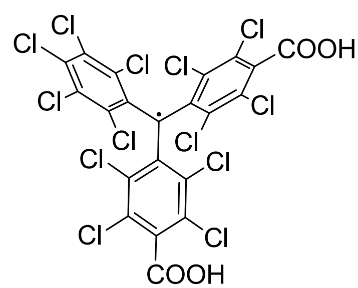

Figure 24. TAM23 chemical structure.

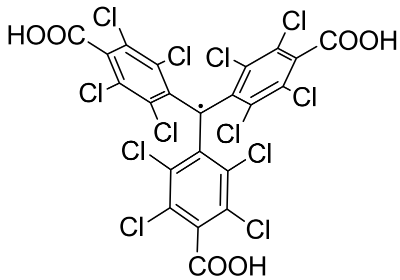

Figure 25. TAM24 chemical structure.

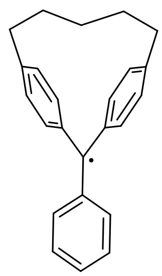

Figure 26. TAM25 chemical structure.

The structural atomic coordinates of our designed radicals TAM**26** and TAM**27,** having highly perpendicular aryl ring configurations, are given below.

Structural Atomic Coordinates

TAM**26**

XYZ
34

H	4.962125240	13.710363837	13.874895422
H	15.010203989	12.355333046	12.972899092
H	10.587113487	5.348436933	12.771386008
H	11.264243791	10.955918902	11.014937746
C	13.846299000	12.049945000	13.026343000
C	13.141177000	12.171442000	14.233277000
C	13.138748000	11.656260000	11.894974000
C	11.789500000	11.848529000	14.283200000
C	11.775101000	11.328419000	11.948810000
C	11.057428000	11.368630000	13.174336000
C	5.966784000	13.111349000	13.667311000
C	6.023144000	11.955768000	12.887718000
C	7.148441000	13.485290000	14.302242000
C	7.185903000	11.192271000	12.759187000
C	8.342449000	12.770757000	14.152253000
C	8.439948000	11.559912000	13.374140000
C	9.670555000	10.790985000	13.224815000
C	9.758177000	9.296026000	13.094428000
C	10.317309000	8.543835000	14.162145000
C	9.449990000	8.552136000	11.933467000
C	10.621230000	7.182031000	14.009935000
C	9.751668000	7.203581000	11.779117000
C	10.374693000	6.501232000	12.822034000
H	13.635783000	12.541311000	15.131315000
H	13.629670000	11.596991000	10.923025000
H	5.136833000	11.637547000	12.334932000
H	7.149781000	14.353940000	14.963635000
H	11.056082000	6.667524000	14.867472000
H	9.476046000	6.696675000	10.854340000
H	10.572685110	9.118786899	15.180285587
S	9.634918000	13.592290000	15.046762000
S	10.883645000	12.134199000	15.783521000
S	8.542385000	9.389249000	10.657280000
S	6.848675000	9.764108000	11.761376000

TAM**27**

XYZ
58

H	-0.00002200	-4.90133600	-2.18911000
H	0.00001700	0.53867900	5.33500300
H	0.00005700	4.37088300	-3.11411400
H	-2.54524200	-2.01696800	1.44943700

H	-4.03758900	-1.27060900	0.91116700
C	-2.94096400	-0.14812600	-1.46147000
C	-2.94649200	1.33516100	0.59900900
C	-2.94393500	-1.19015600	0.85399700
C	-2.57953700	1.23555900	-0.89230700
C	-2.57934900	-1.39008200	-0.62784200
C	-2.58119800	0.15253600	1.51326300
C	-0.00005200	0.42960200	4.25522900
C	-1.19435000	0.35956100	3.55800000
C	1.19427700	0.35949400	3.55801200
C	-1.21829400	0.21893200	2.16899500
C	1.21826400	0.21887600	2.16902200
C	-0.00001800	0.14783400	1.47036500
C	-0.00003000	3.48540300	-2.48659400
C	1.19437700	2.91335500	-2.08187900
C	-1.19441200	2.91330500	-2.08196300
C	1.21781400	1.77482000	-1.27402700
C	-1.21781700	1.77475900	-1.27409900
C	-0.00000800	1.20284900	-0.86696500
C	-0.00000300	-0.00089400	-0.00426700
C	0.00002400	-1.35222100	-0.61072700
C	-1.21782200	-1.99368800	-0.89656000
C	1.21786400	-1.99363200	-0.89661300
C	-1.19434000	-3.26908500	-1.46416100
C	1.19444000	-3.26904300	-1.46423500
C	0.00007100	-3.90964200	-1.74822200
H	-2.13570100	0.41457300	4.09757300
H	2.13559900	0.41445500	4.09764100
H	2.13588400	3.35489600	-2.39631200
H	-2.13594300	3.35476700	-2.39643300
H	-2.13577400	-3.76422000	-1.68514600
H	2.13591200	-3.76409000	-1.68525200
H	-4.03438700	-0.15832500	-1.56206700
H	-2.54043600	-0.25024700	-2.47454600
H	-4.04049200	1.42197100	0.63730000
H	-2.55120500	2.26555200	1.01767200
H	-3.27391100	0.23709500	2.35806900
H	-3.27284700	-2.16356200	-0.97654000
H	-3.27278300	1.92354200	-1.38918000
H	3.27277100	1.92368600	-1.38901700
H	3.27387100	0.23700500	2.35813400
H	3.27290100	-2.16344100	-0.97662600
H	2.54050000	-0.25005300	-2.47452900
H	4.03442500	-0.15817100	-1.56200100
H	2.55112300	2.26553400	1.01784300
H	4.04044700	1.42202900	0.63744700
C	2.57938200	-1.38999900	-0.62789100
C	2.58117300	0.15248900	1.51330900
C	2.57953200	1.23565500	-0.89219900
C	2.94394600	-1.19015400	0.85396800
C	2.94099900	-0.14799000	-1.46143400
C	2.94645100	1.33518200	0.59913200

H	4.03760100	-1.27058300	0.91115400
H	2.54526100	-2.01700900	1.44935200