Electronic Supplementary Information

Contents

DFT Calculations

The DFT calculations were performed using Gaussian 16 [1] running mostly on the Compute Canada Cedar cluster but with some calculations run on a local Windows 10 machine.

The structures were optimized at the UB3LYP/6-311+G(d,p) level with tight convergence criteria. The hyperfine coupling constants (hfccs) were calculated using the same density functional and basis set used in the optimization. Muonium was treated as an isotope of H with mass 0.113429 u and magnetic moment 8.890597 μ_N. Vibrational-averaging effects were included by calculating the anharmonic vibrational frequencies and using the Fermi keyword. The values reported here are the vibrationally-averaged values at 0 K. The advantage of this methodology is that there are no empirical factors needed, but it is very computationally expensive.

C_6H_6Mu radical

The DFT calculations were benchmarked using the muoniated cyclohexadienyl radical, which is formed by Mu addition to benzene. The calculated hfccs at 0 K and the experimental hfccs at 298 K are compared in Table S.1.

Input file

```
%mem=120GB
%nprocs=48
%chk=C6H6Mu-fermi.chk
# freq=(Anharmonic,Readanharm) ub3lyp/6-311+g(d,p) geom=connectivity scf=tight

Fermi calculation of the muoniated cyclohexadienyl radical

0 2
 C              -0.74010300   -1.22506600   -0.00000400
 C               0.62358400   -1.25512500   -0.00001500
 C               1.44710500   -0.00000100    0.00001700
 C               0.62358500    1.25512400   -0.00001500
 C              -0.74010100    1.22506700   -0.00000400
 C              -1.45418800    0.00000100    0.00001400
 H              -1.29446000   -2.15831200   -0.00001600
 H               1.14944000   -2.20416100   -0.00003700
 H               2.13393200   -0.00000100   -0.86539400
 H               1.14944300    2.20415900   -0.00003700
 H              -1.29445700    2.15831300   -0.00001600
 H              -2.53703500    0.00000200    0.00002700
 H(Iso=0.113429,NMagM=8.890597)              2.13384100   -0.00000100    0.86550500

 1 2 2.0 6 1.5 7 1.0
 2 3 1.0 8 1.0
 3 4 1.0 9 1.0 13 1.0
 4 5 2.0 10 1.0
 5 6 1.5 11 1.0
 6 12 1.0
 7
 8
 9
 10
 11
 12
 13

Property=Fermi
```

Optimized structure

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.225065	-0.697462	0.003202
2	6	0	-1.255126	0.665985	-0.022405
3	6	0	-0.000004	1.489362	-0.037908
4	6	0	1.255123	0.665990	-0.022405
5	6	0	1.225068	-0.697455	0.003202
6	6	0	0.000004	-1.411419	0.016599
7	1	0	-2.158310	-1.251723	0.013629
8	1	0	-2.204163	1.191746	-0.032262
9	1	0	-0.000005	2.192326	0.814448
10	1	0	2.204157	1.191758	-0.032262
11	1	0	2.158315	-1.251712	0.013629
12	1	0	0.000007	-2.494075	0.036929
13	1	0	-0.000005	2.159718	-0.916144

Isotropic hyperfine coupling constants

Temperature: 0K

	Atom	Isotropic Fermi Contact Couplings a.u.	MegaHertz	Gauss	10(-4) cm-1	
1	C(13)	-0.03103	-34.88842	-12.44905	-11.63752	
2	C(13)	0.03460	38.90104	13.88086	12.97599	
3	C(13)	-0.03143	-35.33293	-12.60767	-11.78580	
4	C(13)	0.03461	38.90317	13.88162	12.97670	
5	C(13)	-0.03103	-34.88751	-12.44873	-11.63722	
6	C(13)	0.04338	48.76917	17.40205	16.26764	
7	H(1)	0.00224	9.99472	3.56637	3.33388	
8	H(1)	-0.00593	-26.49161	-9.45287	-8.83665	
9	H(1)	0.03026	**135.24608**	48.25916	45.11324	**methylene proton**
10	H(1)	-0.00593	-26.49233	-9.45312	-8.83689	
11	H(1)	0.00224	9.99372	3.56601	3.33355	
12	H(1)	-0.00753	-33.67369	-12.01561	-11.23233	
13	H(1)	0.03847	**547.37069**	195.31547	182.58321	**muon**

Anisotropic hyperfine coupling constants

Temperature: 0K

Anisotropic Spin Dipole Couplings in Principal Axis System

Atom		a.u.	MegaHertz	Gauss	10(-4) cm-1	Axes			
	Baa	-0.1645	-22.077	-7.878	-7.364	0.0145	0.0139	0.9998	
1 C(13)	Bbb	0.0689	9.244	3.299	3.084	0.8856	0.4640	-0.0193	
	Bcc	0.0956	12.832	4.579	4.280	-0.4641	0.8857	-0.0055	
	Baa	-0.2334	-31.318	-11.175	-10.447	0.2564	0.9665	-0.0133	
2 C(13)	Bbb	-0.2148	-28.830	-10.287	-9.617	0.9665	-0.2565	-0.0127	
	Bcc	0.4482	60.148	21.462	20.063	0.0157	0.0096	0.9998	
	Baa	-0.0107	-1.430	-0.510	-0.477	0.0000	0.9512	-0.3087	
3 C(13)	Bbb	0.0048	0.640	0.228	0.213	1.0000	0.0000	0.0002	
	Bcc	0.0059	0.790	0.282	0.263	-0.0002	0.3087	0.9512	
	Baa	-0.2335	-31.336	-11.181	-10.452	-0.2562	0.9665	-0.0133	
4 C(13)	Bbb	-0.2149	-28.844	-10.292	-9.621	0.9665	0.2564	0.0127	
	Bcc	0.4485	60.180	21.474	20.074	-0.0157	0.0096	0.9998	
	Baa	-0.1646	-22.085	-7.880	-7.367	-0.0145	0.0139	0.9998	
5 C(13)	Bbb	0.0689	9.248	3.300	3.085	0.8855	-0.4643	0.0193	
	Bcc	0.0957	12.837	4.581	4.282	0.4644	0.8856	-0.0055	
	Baa	-0.3001	-40.267	-14.368	-13.432	1.0000	-0.0001	0.0000	
6 C(13)	Bbb	-0.2738	-36.743	-13.111	-12.256	0.0001	1.0000	-0.0049	
	Bcc	0.5739	77.010	27.479	25.688	-0.0000	0.0049	1.0000	
	Baa	-0.0071	-3.803	-1.357	-1.269	0.0026	0.0028	1.0000	
7 H(1)	Bbb	-0.0017	-0.931	-0.332	-0.310	0.8432	0.5375	-0.0037	
	Bcc	0.0089	4.734	1.689	1.579	-0.5375	0.8432	-0.0010	
	Baa	-0.0280	-14.943	-5.332	-4.984	0.4716	0.8817	-0.0125	
8 H(1)	Bbb	-0.0022	-1.163	-0.415	-0.388	0.0194	0.0038	0.9998	
	Bcc	0.0302	16.106	5.747	5.372	0.8816	-0.4717	-0.0153	
	Baa	-0.0065	**-3.444**	-1.229	-1.149	0.0001	-0.3976	0.9175	
9 H(1)	Bbb	-0.0002	**-0.128**	-0.046	-0.043	1.0000	-0.0000	-0.0001	**methylene proton**
	Bcc	0.0067	**3.572**	1.275	1.192	0.0001	0.9175	0.3976	
	Baa	-0.0280	-14.946	-5.333	-4.985	-0.4715	0.8818	-0.0125	
10 H(1)	Bbb	-0.0022	-1.165	-0.416	-0.389	-0.0194	0.0039	0.9998	
	Bcc	0.0302	16.111	5.749	5.374	0.8817	0.4717	0.0153	

	Baa	-0.0071	-3.804	-1.357	-1.269	-0.0026	0.0028	1.0000
11 H(1)	Bbb	-0.0017	-0.932	-0.333	-0.311	0.8427	-0.5383	0.0037
	Bcc	0.0089	4.736	1.690	1.580	0.5383	0.8427	-0.0010
	Baa	-0.0372	-19.859	-7.086	-6.624	1.0000	-0.0001	0.0000
12 H(1)	Bbb	0.0005	0.261	0.093	0.087	-0.0000	0.0079	1.0000
	Bcc	0.0367	19.598	6.993	6.537	0.0001	1.0000	-0.0079
	Baa	-0.0052	**-8.909**	-3.179	-2.972	-0.0001	0.4956	0.8686
13 H(1)	Bbb	0.0002	**0.358**	0.128	0.119	1.0000	-0.0000	0.0001 **muon**
	Bcc	0.0050	**8.551**	3.051	2.852	0.0001	0.8686	-0.4956

Table S.1: Experimental isotropic hfccs at 298 K [2,3] and calculated isotropic hfccs of the muoniated cyclohexadienyl radical and the absolute percent difference between these values.

	Experimental Hfcc (MHz)	Calculated Hfcc (MHz)	Absolute % Difference
A_μ	514.409(13)	547.4	6.4
A_p (H6)	126.11(4)	135.2	7.2
A_p (H1,H5)	-25.14(4)	-26.5	5.4
A_p (H2,H4)	7.47(4)	10.0	33.9
A_p (H3)	-36.19(4)	-33.7	6.9

There is reasonably good agreement between the calculated and experimental values of the isotropic hfccs for every nucleus except for the meta protons, where the proton hfcc is relatively small. The calculated values are about 6-7 % larger than the experimental values. This is very good agreement given that there are no empirical factors in the calculation and suggests that the computational methodology is suitable for calculating isotropic muon and methylene proton hfccs in a muoniated cyclohexadienyl radical.

There is also good agreement between the calculated and experimental dipolar hfccs. There is a large positive principal component of +8.551 MHz that was oriented at an angle of 30° with respect to the molecular plane, which roughly corresponds to the direction of the C-Mu bond. This was nearly balanced by a negative out-of-plane component of -8.909 MHz, which leaves only a small in-plane principal component of +0.358 MHz. Roduner et al. used the values determined for the Mu adduct of durene and suggested that the principal components of the muon hyperfine tensor of the C_6H_6Mu radical should be +9.4, -10.4, and +1.0 MHz, respectively.[4] The calculated angle of 30° is slightly higher than the of 25° found in the Mu adduct of durene.[5]

3-Mu-246TMB- radical^{-}

The optimized structure of 3-Mu-246TMB- has different amounts of spin density on the methylene protons due to the position of the methyl groups. At the temperatures where these measurements were performed, the methyl groups should be freely rotating. To mimic this, we averaged the two structures.

3-Mu-246TMB- radical^{-} isomer 1

Input file

```
%mem=120GB
%nprocs=48
%chk=3-Mu-246TBA-freq1-vacuum.chk
# freq=(Anharmonic,Readanharm) ub3lyp/6-311+g(d,p) geom=connectivity scf=tight

Fermi calculation of 3-Mu-246TBA anion in a vacuum

-1 2
 C                  1.56821100    1.23375400    0.09197500
 C                  0.06153500    1.20267100    0.04522400
 C                 -0.63576200    0.02344600   -0.01147300
 C                  0.06341800   -1.22784600   -0.06307800
 C                  1.48034300   -1.23571500   -0.07583800
 C                  2.24250600   -0.10186300   -0.00559400
 H(Iso=0.113429,NMagM=8.890597)    1.94611300    1.90093600   -0.71061100
 H                  1.98567700   -2.19906400   -0.14213800
 C                 -2.18366800    0.00632800    0.00447400
 O                 -2.68843600   -0.47616900    1.04588100
 O                 -2.75216700    0.46494300   -1.01346800
 H                  1.89960700    1.75083000    1.01842600
 C                  3.74205100   -0.12118400   -0.01274500
 H                  4.15782700    0.33816200    0.89691800
 H                  4.13127300   -1.14132700   -0.08072300
 H                  4.15136000    0.45294700   -0.85776300
 C                 -0.69618600   -2.52570100   -0.11210000
 H                 -1.32782800   -2.63624200    0.77461400
 H                 -1.37786500   -2.55336400   -0.97062000
 H                 -0.01476400   -3.37962800   -0.18460500
 C                 -0.60054400    2.54994300    0.08981800
 H                 -0.22721100    3.19332100   -0.72088600
 H                 -1.68117700    2.46857500   -0.01732600
 H                 -0.36961100    3.07167600    1.03143800

1 2 1.0 6 1.0 7 1.0 12 1.0
2 3 2.0 21 1.0
3 4 1.5 9 1.0
4 5 1.5 17 1.0
5 6 2.0 8 1.0
6 13 1.0
7
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8
9 10 2.0 11 2.0
10
11
12
13 14 1.0 15 1.0 16 1.0
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17 18 1.0 19 1.0 20 1.0
18
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21 22 1.0 23 1.0 24 1.0
22
23
24

Property=Fermi

Optimized structure

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.568211	1.233754	0.091975
2	6	0	0.061535	1.202671	0.045224
3	6	0	-0.635762	0.023446	-0.011473
4	6	0	0.063418	-1.227846	-0.063078
5	6	0	1.480343	-1.235715	-0.075838
6	6	0	2.242506	-0.101863	-0.005594
7	1	0	1.946113	1.900936	-0.710611
8	1	0	1.985677	-2.199064	-0.142138
9	6	0	-2.183668	0.006328	0.004474
10	8	0	-2.688436	-0.476169	1.045881
11	8	0	-2.752167	0.464943	-1.013468
12	1	0	1.899607	1.750830	1.018426
13	6	0	3.742051	-0.121184	-0.012745
14	1	0	4.157827	0.338162	0.896918
15	1	0	4.131273	-1.141327	-0.080723
16	1	0	4.151360	0.452947	-0.857763
17	6	0	-0.696186	-2.525701	-0.112100
18	1	0	-1.327828	-2.636242	0.774614
19	1	0	-1.377865	-2.553364	-0.970620
20	1	0	-0.014764	-3.379628	-0.184605
21	6	0	-0.600544	2.549943	0.089818

22	1	0	-0.227211	3.193321	-0.720886
23	1	0	-1.681177	2.468575	-0.017326
24	1	0	-0.369611	3.071676	1.031438

Isotropic hyperfine coupling constant

Temperature: 0K

Isotropic Fermi Contact Couplings

Atom	a.u.	MegaHertz	Gauss	10(-4) cm-1	
1 C(13)	-0.02805	-31.53576	-11.25274	-10.51920	
2 C(13)	0.03031	34.07331	12.15820	11.36563	
3 C(13)	-0.02748	-30.88738	-11.02138	-10.30292	
4 C(13)	0.04016	45.14458	16.10871	15.05861	
5 C(13)	-0.03078	-34.60753	-12.34883	-11.54383	
6 C(13)	0.03394	38.16056	13.61664	12.72899	
7 H(1)	0.03220	**458.16510**	163.48470	152.82743	**muon**
8 H(1)	0.00207	9.25364	3.30193	3.08668	
9 C(13)	0.00316	3.55583	1.26881	1.18610	
10 O(17)	-0.00113	0.68798	0.24549	0.22949	
11 O(17)	-0.00082	0.50009	0.17844	0.16681	
12 H(1)	0.02560	**114.44697**	40.83752	38.17540	**methylene proton**
13 C(13)	-0.01373	-15.43688	-5.50826	-5.14919	
14 H(1)	0.00767	34.26898	12.22802	11.43090	
15 H(1)	0.00060	2.68610	0.95847	0.89599	
16 H(1)	0.00785	35.09383	12.52235	11.70604	
17 C(13)	-0.01638	-18.41399	-6.57057	-6.14225	
18 H(1)	0.01179	52.70375	18.80601	17.58008	
19 H(1)	0.01150	51.42087	18.34825	17.15216	
20 H(1)	0.00109	4.87764	1.74046	1.62701	
21 C(13)	-0.01159	-13.03487	-4.65117	-4.34796	
22 H(1)	0.00652	29.12162	10.39132	9.71393	
23 H(1)	0.00060	2.68049	0.95647	0.89412	
24 H(1)	0.00684	30.58638	10.91398	10.20252	

Anisotropic hyperfine coupling constant

Temperature: 0K

Anisotropic Spin Dipole Couplings in Principal Axis System

Atom	a.u.	MegaHertz	Gauss	10(-4) cm-1	Axes		
	Baa	-0.0166	-2.227	-0.795	-0.743	-0.1417	-0.2964	0.9445
1 C(13)	Bbb	0.0018	0.242	0.086	0.081	0.4729	0.8179	0.3277
	Bcc	0.0148	1.984	0.708	0.662	0.8696	-0.4931	-0.0243

	Baa	-0.2187	-29.342	-10.470	-9.788	0.6053	0.7943	0.0524
2 C(13)	Bbb	-0.2061	-27.650	-9.866	-9.223	0.7960	-0.6037	-0.0433
	Bcc	0.4247	56.992	20.336	19.011	0.0028	-0.0679	0.9977
	Baa	-0.1516	-20.342	-7.259	-6.786	0.0076	-0.0668	0.9977
3 C(13)	Bbb	0.0662	8.877	3.168	2.961	0.9982	-0.0592	-0.0116
	Bcc	0.0854	11.465	4.091	3.824	0.0599	0.9960	0.0662
	Baa	-0.2859	-38.368	-13.691	-12.798	0.8398	-0.5414	-0.0408
4 C(13)	Bbb	-0.2726	-36.585	-13.054	-12.203	0.5429	0.8380	0.0544
	Bcc	0.5586	74.953	26.745	25.002	0.0047	-0.0678	0.9977
	Baa	-0.1520	-20.398	-7.279	-6.804	-0.0068	-0.0613	0.9981
5 C(13)	Bbb	0.0622	8.348	2.979	2.785	-0.4947	0.8676	0.0499
	Bcc	0.0898	12.050	4.300	4.020	0.8690	0.4935	0.0362
	Baa	-0.2362	-31.692	-11.308	-10.571	0.3843	0.9212	0.0611
6 C(13)	Bbb	-0.2239	-30.047	-10.722	-10.023	0.9230	-0.3847	-0.0056
	Bcc	0.4601	61.739	22.030	20.594	-0.0183	-0.0586	0.9981
	Baa	-0.0049	**-8.350**	-2.980	-2.785	0.1700	0.2652	0.9491
7 H(1)	Bbb	0.0019	**3.169**	1.131	1.057	0.9357	-0.3454	-0.0710 **muon**
	Bcc	0.0031	**5.181**	1.849	1.728	0.3090	0.9002	-0.3069
	Baa	-0.0071	-3.769	-1.345	-1.257	-0.0066	-0.0800	0.9968
8 H(1)	Bbb	-0.0016	-0.840	-0.300	-0.280	-0.3570	0.9313	0.0724
	Bcc	0.0086	4.609	1.645	1.538	0.9341	0.3554	0.0347
	Baa	-0.0064	-0.857	-0.306	-0.286	0.0109	-0.2766	0.9609
9 C(13)	Bbb	0.0013	0.173	0.062	0.058	0.1339	0.9527	0.2728
	Bcc	0.0051	0.684	0.244	0.228	0.9909	-0.1257	-0.0474
	Baa	-0.0382	2.768	0.988	0.923	0.9117	0.2312	0.3396
10 O(17)	Bbb	0.0175	-1.266	-0.452	-0.422	-0.1988	-0.4752	0.8571
	Bcc	0.0208	-1.501	-0.536	-0.501	-0.3596	0.8490	0.3873
	Baa	-0.0343	2.481	0.885	0.827	0.8386	-0.3214	-0.4398
11 O(17)	Bbb	0.0155	-1.118	-0.399	-0.373	0.4875	0.0826	0.8692
	Bcc	0.0188	-1.362	-0.486	-0.454	0.2431	0.9433	-0.2259
	Baa	-0.0053	**-2.807**	-1.001	-0.936	-0.1800	-0.3537	0.9179
12 H(1)	Bbb	0.0016	**0.840**	0.300	0.280	0.9058	-0.4235	0.0144 **methylene proton**
	Bcc	0.0037	**1.967**	0.702	0.656	0.3837	0.8340	0.3966
	Baa	-0.0061	-0.820	-0.293	-0.274	-0.0340	-0.1140	0.9929
13 C(13)	Bbb	-0.0038	-0.516	-0.184	-0.172	0.1163	0.9863	0.1172
	Bcc	0.0100	1.336	0.477	0.446	0.9926	-0.1194	0.0203

	Baa	-0.0041	-2.162	-0.771	-0.721	-0.2641	0.2471	0.9323
14 H(1)	Bbb	-0.0034	-1.793	-0.640	-0.598	0.0013	0.9667	-0.2558
	Bcc	0.0074	3.954	1.411	1.319	0.9645	0.0664	0.2556
	Baa	-0.0042	-2.229	-0.795	-0.743	0.4430	0.8927	0.0820
15 H(1)	Bbb	-0.0031	-1.634	-0.583	-0.545	-0.0246	-0.0793	0.9965
	Bcc	0.0072	3.863	1.378	1.288	0.8962	-0.4435	-0.0132
	Baa	-0.0041	-2.185	-0.780	-0.729	0.2170	-0.0932	0.9717
16 H(1)	Bbb	-0.0033	-1.743	-0.622	-0.581	-0.0493	0.9931	0.1062
	Bcc	0.0074	3.928	1.402	1.310	0.9749	0.0709	-0.2109
	Baa	-0.0086	-1.153	-0.412	-0.385	0.8749	-0.4843	0.0055
17 C(13)	Bbb	0.0016	0.215	0.077	0.072	0.0050	0.0202	0.9998
	Bcc	0.0070	0.938	0.335	0.313	0.4843	0.8747	-0.0201
	Baa	-0.0044	-2.324	-0.829	-0.775	0.7223	-0.5188	0.4574
18 H(1)	Bbb	-0.0035	-1.873	-0.668	-0.625	-0.1893	0.4878	0.8522
	Bcc	0.0079	4.196	1.497	1.400	0.6652	0.7021	-0.2541
	Baa	-0.0042	-2.264	-0.808	-0.755	0.7074	-0.4633	-0.5338
19 H(1)	Bbb	-0.0036	-1.934	-0.690	-0.645	0.2079	-0.5854	0.7836
	Bcc	0.0079	4.198	1.498	1.400	0.6755	0.6653	0.3178
	Baa	-0.0043	-2.273	-0.811	-0.758	0.9974	-0.0706	-0.0136
20 H(1)	Bbb	-0.0035	-1.859	-0.663	-0.620	0.0092	-0.0620	0.9980
	Bcc	0.0077	4.132	1.474	1.378	0.0713	0.9956	0.0612
	Baa	-0.0051	-0.680	-0.243	-0.227	-0.0762	-0.1294	0.9887
21 C(13)	Bbb	-0.0037	-0.492	-0.175	-0.164	0.8304	0.5406	0.1348
	Bcc	0.0087	1.172	0.418	0.391	-0.5519	0.8313	0.0663
	Baa	-0.0039	-2.092	-0.747	-0.698	0.0125	0.1924	0.9812
22 H(1)	Bbb	-0.0030	-1.609	-0.574	-0.537	0.9177	0.3876	-0.0877
	Bcc	0.0069	3.701	1.321	1.235	-0.3972	0.9015	-0.1717
	Baa	-0.0039	-2.106	-0.752	-0.703	0.5899	0.8011	0.1018
23 H(1)	Bbb	-0.0030	-1.607	-0.573	-0.536	-0.0400	-0.0969	0.9945
	Bcc	0.0070	3.713	1.325	1.239	0.8065	-0.5907	-0.0252
	Baa	-0.0039	-2.061	-0.735	-0.687	0.2563	-0.2201	0.9412
24 H(1)	Bbb	-0.0031	-1.673	-0.597	-0.558	0.8832	0.4490	-0.1354
	Bcc	0.0070	3.733	1.332	1.245	-0.3928	0.8660	0.3095

3-Mu-246TMB- radical – isomer 2

Input file

```
%nprocshared=6
%chk=3-Mu-246TBA-freq2-vacuum.chk
# freq=(Anharmonic,Readanharm) ub3lyp/6-311+g(d,p) geom=connectivity scf=tight

Fermi calculation of 3-Mu-246TBA anion in a vacuum

-1 2
 C                  1.56821100    1.23375400    0.09197500
 C                  0.06153500    1.20267100    0.04522400
 C                 -0.63576200    0.02344600   -0.01147300
 C                  0.06341800   -1.22784600   -0.06307800
 C                  1.48034300   -1.23571500   -0.07583800
 C                  2.24250600   -0.10186300   -0.00559400
 H                  1.94611300    1.90093600   -0.71061100
 H                  1.98567700   -2.19906400   -0.14213800
 C                 -2.18366800    0.00632800    0.00447400
 O                 -2.68843600   -0.47616900    1.04588100
 O                 -2.75216700    0.46494300   -1.01346800
 H(Iso=0.113429,NMagM=8.890597)    1.89960700    1.75083000    1.01842600
 C                  3.74205100   -0.12118400   -0.01274500
 H                  4.15782700    0.33816200    0.89691800
 H                  4.13127300   -1.14132700   -0.08072300
 H                  4.15136000    0.45294700   -0.85776300
 C                 -0.69618600   -2.52570100   -0.11210000
 H                 -1.32782800   -2.63624200    0.77461400
 H                 -1.37786500   -2.55336400   -0.97062000
 H                 -0.01476400   -3.37962800   -0.18460500
 C                 -0.60054400    2.54994300    0.08981800
 H                 -0.22721100    3.19332100   -0.72088600
 H                 -1.68117700    2.46857500   -0.01732600
 H                 -0.36961100    3.07167600    1.03143800

1 2 1.0 6 1.0 7 1.0 12 1.0
2 3 2.0 21 1.0
3 4 1.5 9 1.0
4 5 1.5 17 1.0
5 6 2.0 8 1.0
6 13 1.0
7
8
9 10 2.0 11 2.0
10
11
```

12
13 14 1.0 15 1.0 16 1.0
14
15
16
17 18 1.0 19 1.0 20 1.0
18
19
20
21 22 1.0 23 1.0 24 1.0
22
23
24

Property=Fermi

Optimized structure

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.568211	1.233754	0.091975
2	6	0	0.061535	1.202671	0.045224
3	6	0	-0.635762	0.023446	-0.011473
4	6	0	0.063418	-1.227846	-0.063078
5	6	0	1.480343	-1.235715	-0.075838
6	6	0	2.242506	-0.101863	-0.005594
7	1	0	1.946113	1.900936	-0.710611
8	1	0	1.985677	-2.199064	-0.142138
9	6	0	-2.183668	0.006328	0.004474
10	8	0	-2.688436	-0.476169	1.045881
11	8	0	-2.752167	0.464943	-1.013468
12	1	0	1.899607	1.750830	1.018426
13	6	0	3.742051	-0.121184	-0.012745
14	1	0	4.157827	0.338162	0.896918
15	1	0	4.131273	-1.141327	-0.080723
16	1	0	4.151360	0.452947	-0.857763
17	6	0	-0.696186	-2.525701	-0.112100
18	1	0	-1.327828	-2.636242	0.774614
19	1	0	-1.377865	-2.553364	-0.970620
20	1	0	-0.014764	-3.379628	-0.184605
21	6	0	-0.600544	2.549943	0.089818
22	1	0	-0.227211	3.193321	-0.720886
23	1	0	-1.681177	2.468575	-0.017326
24	1	0	-0.369611	3.071676	1.031438

Isotropic hyperfine coupling constants

Temperature: 0K

Isotropic Fermi Contact Couplings

	Atom	a.u.	MegaHertz	Gauss	10(-4) cm-1	
1	C(13)	-0.02798	-31.46018	-11.22578	-10.49399	
2	C(13)	0.03028	34.04443	12.14790	11.35600	
3	C(13)	-0.02758	-31.00937	-11.06491	-10.34361	
4	C(13)	0.04003	44.99720	16.05612	15.00945	
5	C(13)	-0.03078	-34.59943	-12.34594	-11.54113	
6	C(13)	0.03412	38.35181	13.68488	12.79279	
7	H(1)	0.02543	**113.66069**	40.55696	37.91312	**methylene proton**
8	H(1)	0.00207	9.26993	3.30774	3.09212	
9	C(13)	0.00315	3.53602	1.26174	1.17949	
10	O(17)	-0.00123	0.74379	0.26540	0.24810	
11	O(17)	-0.00058	0.34939	0.12467	0.11654	
12	H(1)	0.03256	**463.23089**	165.29230	154.51719	**muon**
13	C(13)	-0.01379	-15.50158	-5.53135	-5.17077	
14	H(1)	0.00786	35.12494	12.53345	11.71642	
15	H(1)	0.00061	2.70779	0.96621	0.90322	
16	H(1)	0.00767	34.26968	12.22827	11.43114	
17	C(13)	-0.01620	-18.21522	-6.49964	-6.07594	
18	H(1)	0.01052	47.01467	16.77600	15.68241	
19	H(1)	0.01275	57.00684	20.34146	19.01544	
20	H(1)	0.00104	4.64276	1.65665	1.54866	
21	C(13)	-0.01154	-12.97451	-4.62963	-4.32783	
22	H(1)	0.00651	29.11562	10.38918	9.71192	
23	H(1)	0.00062	2.79066	0.99578	0.93086	
24	H(1)	0.00682	30.47359	10.87373	10.16490	

Anisotropic hyperfine coupling constants

Temperature: 0K

Anisotropic Spin Dipole Couplings in Principal Axis System

Atom	a.u.	MegaHertz	Gauss	10(-4) cm-1	Axes		
	Baa	-0.0174	-2.338	-0.834	-0.780	0.1211	0.1433	0.9822
1 C(13)	Bbb	0.0023	0.303	0.108	0.101	0.4801	0.8576	-0.1843
	Bcc	0.0152	2.035	0.726	0.679	0.8688	-0.4939	-0.0351
	Baa	-0.2189	-29.373	-10.481	-9.798	0.6067	0.7928	0.0579
2 C(13)	Bbb	-0.2058	-27.614	-9.853	-9.211	0.7947	-0.6066	-0.0220
	Bcc	0.4247	56.987	20.334	19.009	-0.0177	-0.0594	0.9981

	Baa	-0.1515	-20.326	-7.253	-6.780	-0.0166	-0.0577	0.9982	
3 C(13)	Bbb	0.0664	8.916	3.182	2.974	0.9959	-0.0895	0.0114	
	Bcc	0.0850	11.410	4.071	3.806	0.0887	0.9943	0.0590	
	Baa	-0.2846	-38.191	-13.627	-12.739	0.8304	-0.5554	-0.0439	
4 C(13)	Bbb	-0.2711	-36.377	-12.980	-12.134	0.5570	0.8297	0.0380	
	Bcc	0.5557	74.568	26.608	24.873	0.0153	-0.0560	0.9983	
	Baa	-0.1516	-20.349	-7.261	-6.788	0.0154	-0.0689	0.9975	
5 C(13)	Bbb	0.0621	8.331	2.973	2.779	-0.4866	0.8710	0.0677	
	Bcc	0.0896	12.018	4.288	4.009	0.8735	0.4864	0.0202	
	Baa	-0.2357	-31.632	-11.287	-10.551	0.4088	0.9104	0.0640	
6 C(13)	Bbb	-0.2232	-29.945	-10.685	-9.988	0.9126	-0.4068	-0.0422	
	Bcc	0.4589	61.576	21.972	20.540	0.0123	-0.0756	0.9971	
	Baa	-0.0051	**-2.733**	-0.975	-0.912	0.1717	0.2375	0.9561	
7 H(1)	Bbb	0.0016	**0.833**	0.297	0.278	0.9114	-0.4066	-0.0627	**methylene proton**
	Bcc	0.0036	**1.900**	0.678	0.634	0.3739	0.8822	-0.2863	
	Baa	-0.0070	-3.753	-1.339	-1.252	0.0206	-0.0780	0.9967	
8 H(1)	Bbb	-0.0016	-0.837	-0.299	-0.279	-0.3445	0.9353	0.0803	
	Bcc	0.0086	4.590	1.638	1.531	0.9386	0.3450	0.0076	
	Baa	-0.0064	-0.864	-0.308	-0.288	-0.0071	-0.2713	0.9625	
9 C(13)	Bbb	0.0012	0.166	0.059	0.055	0.1623	0.9494	0.2688	
	Bcc	0.0052	0.699	0.249	0.233	0.9867	-0.1581	-0.0373	
	Baa	-0.0384	2.779	0.992	0.927	0.8992	0.2387	0.3666	
10 O(17)	Bbb	0.0184	-1.329	-0.474	-0.443	-0.1804	-0.5611	0.8079	
	Bcc	0.0200	-1.450	-0.517	-0.484	-0.3985	0.7926	0.4615	
	Baa	-0.0325	2.353	0.840	0.785	0.8192	-0.3737	-0.4350	
11 O(17)	Bbb	0.0140	-1.010	-0.361	-0.337	0.4257	-0.1120	0.8979	
	Bcc	0.0186	-1.343	-0.479	-0.448	0.3843	0.9207	-0.0674	
	Baa	-0.0050	**-8.446**	-3.014	-2.817	-0.1743	-0.3569	0.9177	
12 H(1)	Bbb	0.0019	**3.276**	1.169	1.093	0.9125	-0.4089	0.0143	**muon**
	Bcc	0.0030	**5.170**	1.845	1.724	0.3701	0.8399	0.3969	
	Baa	-0.0061	-0.819	-0.292	-0.273	0.0239	-0.0251	0.9994	
13 C(13)	Bbb	-0.0039	-0.521	-0.186	-0.174	0.1296	0.9913	0.0218	
	Bcc	0.0100	1.340	0.478	0.447	0.9913	-0.1290	-0.0269	
	Baa	-0.0041	-2.166	-0.773	-0.723	-0.2175	-0.0398	0.9753	
14 H(1)	Bbb	-0.0033	-1.753	-0.626	-0.585	-0.0389	0.9987	0.0321	
	Bcc	0.0073	3.920	1.399	1.307	0.9753	0.0310	0.2187	

	Baa	-0.0042	-2.222	-0.793	-0.741	0.4537	0.8899	0.0481
15 H(1)	Bbb	-0.0031	-1.628	-0.581	-0.543	0.0187	-0.0635	0.9978
	Bcc	0.0072	3.849	1.373	1.284	0.8910	-0.4518	-0.0454
	Baa	-0.0040	-2.154	-0.769	-0.719	0.2577	-0.3618	0.8959
16 H(1)	Bbb	-0.0034	-1.795	-0.640	-0.599	0.0090	0.9281	0.3722
	Bcc	0.0074	3.949	1.409	1.317	0.9662	0.0879	-0.2425
	Baa	-0.0085	-1.144	-0.408	-0.382	0.8684	-0.4955	0.0221
17 C(13)	Bbb	0.0016	0.213	0.076	0.071	-0.0297	-0.0076	0.9995
	Bcc	0.0069	0.931	0.332	0.311	0.4951	0.8686	0.0213
	Baa	-0.0043	-2.277	-0.813	-0.760	0.6168	-0.4194	0.6661
18 H(1)	Bbb	-0.0036	-1.944	-0.694	-0.649	-0.3384	0.6227	0.7055
	Bcc	0.0079	4.221	1.506	1.408	0.7106	0.6606	-0.2422
	Baa	-0.0044	-2.368	-0.845	-0.790	0.7470	-0.5042	-0.4333
19 H(1)	Bbb	-0.0034	-1.822	-0.650	-0.608	0.1271	-0.5315	0.8375
	Bcc	0.0079	4.190	1.495	1.398	0.6525	0.6807	0.3330
	Baa	-0.0043	-2.275	-0.812	-0.759	0.9883	-0.0897	0.1237
20 H(1)	Bbb	-0.0034	-1.835	-0.655	-0.612	-0.1262	-0.0220	0.9918
	Bcc	0.0077	4.110	1.467	1.371	0.0862	0.9957	0.0330
	Baa	-0.0050	-0.671	-0.239	-0.224	-0.0036	-0.0427	0.9991
21 C(13)	Bbb	-0.0037	-0.498	-0.178	-0.166	0.8416	0.5395	0.0261
	Bcc	0.0087	1.169	0.417	0.390	-0.5401	0.8409	0.0340
	Baa	-0.0038	-2.035	-0.726	-0.679	-0.2439	0.1164	0.9628
22 H(1)	Bbb	-0.0032	-1.691	-0.603	-0.564	0.9007	0.3951	0.1804
	Bcc	0.0070	3.726	1.329	1.243	-0.3594	0.9112	-0.2013
	Baa	-0.0039	-2.102	-0.750	-0.701	0.6035	0.7963	0.0412
23 H(1)	Bbb	-0.0030	-1.613	-0.575	-0.538	-0.0191	-0.0372	0.9991
	Bcc	0.0070	3.715	1.325	1.239	0.7971	-0.6038	-0.0072
	Baa	-0.0039	-2.094	-0.747	-0.699	-0.0084	-0.3096	0.9508
24 H(1)	Bbb	-0.0030	-1.614	-0.576	-0.538	0.9175	0.3758	0.1304
	Bcc	0.0070	3.708	1.323	1.237	-0.3977	0.8735	0.2809

Rotational Averaging of Muon Dipolar Hyperfine Coupling Constants

The hyperfine tensors obtained from the Gaussian 16 calculations were used to calculate the axial hyperfine tensors that result from rapid uniaxial rotation about an axis. The isotropic muon hfcc, A_μ, the principal muon dipolar hfccs (B_{aa}, B_{bb} and B_{cc}) and the direction cosines (***R***) for the coordinate system where the dipolar tensor is diagonal (a,b,c) were obtained from the calculations.

	B_{aa}	$a_1\ a_2\ a_3$
X H(1)	B_{bb}	$b_1\ b_2\ b_3$
	B_{cc}	$c_1\ c_2\ c_3$

$$\mathbf{B}_{(a,b,c)} = \begin{vmatrix} B_{aa} & 0 & 0 \\ 0 & B_{bb} & 0 \\ 0 & 0 & B_{cc} \end{vmatrix} \quad \textbf{(1.1)}$$

The hyperfine tensor $\mathbf{B}_{(a,b,c)}$ was transformed from the (a,b,c) coordinate system to the (x,y,z) coordinate system of the molecule, $\mathbf{B}_{(x,y,z)}$. This is done using the rotation matrix, **R**, and its transpose, $\mathbf{R}^T$:

$$\mathbf{R} = \begin{vmatrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \\ c_1 & c_2 & c_3 \end{vmatrix} \quad \textbf{(1.2)}$$

$$\mathbf{R}^T = \begin{vmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{vmatrix}. \quad \textbf{(1.3)}$$

$$\mathbf{B}_{(x,y,z)} = \mathbf{R}^T \cdot \mathbf{B}_{(a,b,c)} \cdot \mathbf{R} \quad \textbf{(1.4)}$$

$\mathbf{B}_{(x,y,z)}$ is generally not diagonal. For an arbitrary, normalized rotation axis in the molecular reference frame, **n**:

$$D_X^{\parallel} = \mathbf{n}^T \cdot \mathbf{B}_{(x,y,z)} \cdot \mathbf{n} \quad \textbf{(1.5)}$$

This simplifies to:

$$D_X^{\parallel} = \left(\mathbf{n}^T \cdot \mathbf{a}\right)^2 B_{aa} + \left(\mathbf{n}^T \cdot \mathbf{b}\right)^2 B_{bb} + \left(\mathbf{n}^T \cdot \mathbf{c}\right)^2 B_{cc} \quad \textbf{(1.6)}$$

where

$$\mathbf{a} = \begin{vmatrix} a_1 \\ a_2 \\ a_3 \end{vmatrix}; \mathbf{b} = \begin{vmatrix} b_1 \\ b_2 \\ b_3 \end{vmatrix}; \mathbf{c} = \begin{vmatrix} c_1 \\ c_2 \\ c_3 \end{vmatrix} \quad \textbf{(1.7)}$$

This makes it possible to calculate $D_\mu^{\parallel}$ for any arbitrary rotation axis. The axial dipolar muon hyperfine tensor of the muoniated radicals were calculated for different rotation axes.

As a test we calculated the $D_\mu^{\parallel}$ for the C_6H_6Mu radical undergoing rapid rotation about two different axes: perpendicular to the six-membered ring and parallel to the vector connecting the ipso and para carbons. Fast uniaxial rotation about an axis perpendicular to the molecular plane will result in $D_\mu^{\parallel}$ = -4.62 MHz. Roduner et al. calculated this value to be -6.8 MHz.[4] Fast uniaxial rotation about the axis connecting the ipso and para carbons will result in $D_\mu^{\parallel}$ = +4.26 MHz. Roduner et al. calculated this

value to be +5.8 MHz.[4] The reason for the difference is the slightly different values of the principal components and their orientations. Nevertheless, there is reasonable agreement and the trend in terms of the sign is reproduced.

Solvent Effects on Hyperfine Coupling Constants

The radical anion and the Na^+ - radical anion ion pair were optimized at the UB3LYP/6-311+G(d,p) level using the conductor-like polarizable continuum model (CPCM).

opt=tight ub3lyp/6-311+g(d,p) scrf=(cpcm,solvent=water) geom=connectivity scf=tight

We scaled the computed average proton hfccs of the methylene protons by a factor of 3.82 to predict A_μ (1.20 for the isotope effect and 3.183 for the muon magnetic moment) and a factor of 0.94 for the corresponding A_p of the H in a -CHMu- group.

Solvent	ε	(ε-1)/(2ε+1)	3-Mu-246TMB$^-$		Na^+-3-Mu-246TMB$^-$	
			A_μ (MHz)	A_p (MHz)	A_μ (MHz)	A_p (MHz)
Water	78.36	0.4905	448.07	110.27	448.41	110.35
Methanol	32.61	0.4774	447.78	110.20	448.20	110.30
Ethanol	24.85	0.4704	447.63	110.16	448.09	110.28
1-Pentanol	15.13	0.4520	447.23	110.06	447.82	110.21
1-Nonanol	8.60	0.4176	446.48	109.88	447.33	110.09
n-Methylaniline	5.96	0.3839	445.75	109.70	446.83	109.97
Diethyl ether	4.24	0.3418	444.83	109.47	446.21	109.81
Dibutyl ether	3.05	0.2886	443.67	109.19	445.38	109.61
Carbon disulfide	2.61	0.2589	443.03	109.03	444.86	109.48
Trans-decalin	2.18	0.2200	442.17	108.82	444.00	109.27
Heptane	1.91	0.1890	441.46	108.64	443.36	109.11

Electric Field Calculations

The variation in energy with electric field was calculated as a function of the angle θ, which is the angle between the electric field and the dipole moment of the 3-Mu-246TMB$^-$ radical anion, which is essentially along the x axis of Figure 4. There is very little variation with the angle in the y-z plane. The structures were not optimized. Only single point calculations of the energy were performed on the 3-Mu-246TMB$^-$ radical anion optimized at the UB3LYP/6-311+G(d,p) level.

ub3lyp/6-311+g(d,p) nosymm field=x+20 scf=tight

This applies a field of 0.002 au, or 1.03 x 10^7 V/cm, along the x axis. The input coordinates of the optimized structure were rotated in order to apply the electric field along a given axis.

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