Supplementary Material

to

Flip-Flop Motion of Circular Hydrogen Bond Array in Thiacalix[4]arene

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Table 1: The measured ^{13}C longitudinal relaxation rates R_1 (in s^{-1}) in thiacalix[4]arene.

Temperature (K)	223	233	243	253	263	273	283	293	303	313
C-1	1.28	1.32	1.00	0.831	0.628	0.511	0.382	0.319	0.255	0.198
C-2.C-6	0.903	0.942	0.775	0.577	0.443	0.353	0.272	0.225	0.180	0.159
C-3.C-5	5.39	5.73	5.13	4.41	3.79	3.05	2.64	2.17	1.76	1.42
C-4	5.30	5.37	4.97	4.59	3.85	3.10	2.76	2.25	1.87	1.49

Table 2: The measured ^{13}C transverse relaxation rates R_2 (in s^{-1}) in thiacalix[4]arene.

Temperature (K)	223	233	243	253	263	273	283	293	303	313
C-1	3.12	2.00	1.58	0.98	0.730	0.56	0.55	0.41	0.29	0.23
C-2.C-6	15.06	20.09	16.17	9.11	4.85	2.53	1.59	0.93	0.57	0.39
C-3.C-5	13.61	11.02	8.29	6.15	4.56	3.79	3.01	2.33	1.92	1.68
C-4	12.99	9.70	6.96	4.90	4.39	3.33	3.09	2.34	1.83	1.76

Table 3: The measured $\{^1H\}$ - ^{13}C NOE in thiacalix[4]arene.

Temperature (K)	223	233	243	253	263	273	283	293	303	313
C-1	0.97	1.04	1.10	1.14	1.28	1.38	1.45	1.53	1.47	1.53
C-2.C-6	1.09	1.03	1.10	1.15	1.23	1.31	1.38	1.39	1.42	1.45
C-3.C-5	1.20	1.31	1.53	1.85	2.12	2.33	2.50	2.51	2.60	2.64
C-4	1.12	1.30	1.48	1.73	2.13	2.21	2.44	2.53	2.77	2.55

Table 4: The dependence of the experimental signal intensities (in arbitrary units) of C-2. C-6 resonance on the echo-time t_{echo} and the number of echoes n. The individual series of intensities correspond to the separate CPMG experiments. The intensities are directly comparable within each series. Different series at the same temperature are related through a scaling factor due to the separate measurements and data processing (in practice, the scaling factor is often close to unity).

Temperature 223 K

n	t_{echo} / ms	Intensity
16	0.2	1.9459
32	0.2	1.9179
64	0.2	1.8731
120	0.2	1.7690
240	0.2	1.6779
480	0.2	1.4871
1000	0.2	1.2814
2000	0.2	0.7088

n	t_{echo} / ms	Intensity
4	0.4	2.0674
8	0.4	1.7169
16	0.4	1.6854
32	0.4	1.7521
48	0.4	1.6843
80	0.4	1.5982
120	0.4	1.3592
320	0.4	1.0431
400	0.4	0.7526
800	0.4	0.3498

n	t_{echo} / ms	Intensity
4	0.8	2.0779
8	0.8	1.8607
16	0.8	1.6752
24	0.8	1.3891
32	0.8	1.4363
48	0.8	1.1641
80	0.8	0.7791
160	0.8	0.3423

n	t_{echo} / ms	Intensity
4	1.2	1.6297
8	1.2	1.3766
12	1.2	1.2071
16	1.2	1.1079
20	1.2	0.8477
24	1.2	0.8963
40	1.2	0.5716
64	1.2	0.2603

n	t_{echo} / ms	Intensity
4	1.6	1.5131
8	1.6	1.2556
12	1.6	0.93183
16	1.6	0.57045
24	1.6	0.52867
32	1.6	0.18443
60	1.6	0.15255

n	t_{echo} / ms	Intensity
4	2	1.3364
8	2	1.1038
12	2	0.59302
16	2	0.37061
24	2	0.15849
40	2	0.17211

n	t_{echo} / ms	Intensity
4	3	0.82091
8	3	0.45779
12	3	0.14924
16	3	0.085804

Temperature 233 K

n	t_{echo} / ms	Intensity
4	4.96	0.5732
8	2.46	0.8237
12	1.6271	0.8145
16	1.2104	0.9028
20	0.9604	0.9646
24	0.79373	1.0936
32	0.5854	1.1952
44	0.41495	1.3019
80	0.2104	1.5316

n	t_{echo} / ms	Intensity
16	1.8354	0.9300
20	1.4604	1.0550
24	1.2104	1.1768
28	1.0318	1.3020
36	0.79373	1.5908
48	0.5854	1.8379
68	0.40158	2.2035
88	0.30131	2.4466
120	0.2104	2.4517

n	t_{echo} / ms	Intensity
4	0.8	1.6002
8	0.8	1.5440
16	0.8	1.2862
24	0.8	1.2206
32	0.8	0.9045
48	0.8	0.7951
80	0.8	0.5300
160	0.8	0.1165

Temperature 243 K

n	t_{echo} / ms	Intensity
4	4.96	1.4893
8	2.46	1.4845
12	1.6261	1.5818
16	1.2094	1.5308
20	0.9594	1.4884
24	0.7928	1.6728
32	0.5844	1.6409
44	0.41394	1.8666
60	0.2928	1.8400
80	0.2094	1.9383

n	t_{echo} / ms	Intensity
4	0.8	2.2914
8	0.8	2.0998
12	0.8	1.9720
20	0.8	1.8255
32	0.8	1.4385
64	0.8	1.0810
128	0.8	0.4541
252	0.8	0.0914

Temperature 253 K

n	t_{echo} / ms	Intensity
4	7.4601	1.7622
8	3.7101	1.7805
12	2.4601	1.8112
16	1.8351	1.6667
20	1.4601	1.7289
24	1.2101	1.8304
28	1.0315	1.7434
36	0.7934	1.8451
48	0.5851	1.7388
68	0.4013	1.8111
88	0.301	1.8796
120	0.2101	1.9511

n	t_{echo} / ms	Intensity
4	4.9601	1.9873
8	2.4601	2.0263
12	1.6268	2.056
16	1.2101	2.0446
20	0.9601	1.9649
24	0.79343	2.0643
32	0.5851	1.9152
44	0.41465	2.1051
60	0.29343	2.1254
80	0.2101	2.098

n	t_{echo} / ms	Intensity
4	0.8	1.3756
8	0.8	1.3095
12	0.8	1.2491
20	0.8	1.3446
32	0.8	1.2269
64	0.8	1.2138
128	0.8	1.1638
252	0.8	1.0701
500	0.8	0.8716
1000	0.8	0.5014
2000	0.8	0.36121

Temperature 263 K

n	t_{echo} / ms	Intensity
24	0.79324	2.1577
32	0.5849	2.2702
44	0.41444	2.3591
60	0.29324	2.1510
80	0.2099	2.2530

n	t_{echo} / ms	Intensity
4	0.8	2.8750
8	0.8	2.8341
12	0.8	2.8487
24	0.8	2.5710
48	0.8	2.4162
96	0.8	1.9908
188	0.8	1.3684

Temperature 273 K

n	t_{echo} / ms	Intensity
4	0.2	2.8978
32	0.2	2.697
60	0.2	2.6833
120	0.2	2.6069
240	0.2	2.4406
600	0.2	2.2218
1000	0.2	1.5903
2000	0.2	1.0547
4000	0.2	0.41054
8000	0.2	0.1336

n	t_{echo} / ms	Intensity
1	0.4	2.9394
4	0.4	2.8627
8	0.4	2.8216
15	0.4	2.6779
30	0.4	2.4905
60	0.4	2.2659
120	0.4	1.7627
250	0.4	1.0264
500	0.4	0.3244
1000	0.4	0.067898

n	t_{echo} / ms	Intensity
4	0.6	2.7742
8	0.6	2.6488
24	0.6	2.5761
60	0.6	2.6541
88	0.6	2.4079
176	0.6	2.1579
360	0.6	1.4960
720	0.6	0.9048
1480	0.6	0.2808

n	t_{echo} / ms	Intensity
4	0.8	2.8936
8	0.8	2.8515
16	0.8	2.848
32	0.8	2.7772
64	0.8	2.5946
120	0.8	2.349
240	0.8	1.7339
600	0.8	1.1071
1000	0.8	0.38466

n	t_{echo} / ms	Intensity
2	1.0	2.9192
4	1.0	2.6799
12	1.0	2.6214
24	1.0	2.5157
60	1.0	2.4676
100	1.0	2.0795
200	1.0	1.6396
400	1.0	0.9668
800	1.0	0.3023
1600	1.0	0.0826
6400	1.0	0.0170

n	t_{echo} / ms	Intensity
2	1.2	2.8316
4	1.2	2.7386
8	1.2	2.6803
20	1.2	2.6234
40	1.2	2.3482
80	1.2	2.2002
156	1.2	1.6158
312	1.2	1.0327
624	1.2	0.3391

n	t_{echo} / ms	Intensity
2	1.6	2.8179
4	1.6	2.7182
8	1.6	2.6553
16	1.6	2.4707
32	1.6	2.4099
60	1.6	2.0851
124	1.6	1.6291
248	1.6	0.9147
500	1.6	0.3022

n	t_{echo} / ms	Intensity
2	2.4	2.8745
4	2.4	2.5638
8	2.4	2.5963
16	2.4	2.3672
32	2.4	2.2490
40	2.4	1.9728
80	2.4	1.5397
156	2.4	0.9362
312	2.4	0.3465
624	2.4	0.0969

n	t_{echo} / ms	Intensity
4	3.2	2.5927
8	3.2	2.4790
16	3.2	2.1853
28	3.2	1.9682
56	3.2	1.6339
96	3.2	1.1332
120	3.2	0.8334
240	3.2	0.3254
400	3.2	0.1584

n	t_{echo} / ms	Intensity
2	4.0	2.6853
4	4.0	2.4491
8	4.0	2.2677
12	4.0	2.3124
20	4.0	1.9783
32	4.0	1.8780
64	4.0	1.2658
120	4.0	0.7131
240	4.0	0.1947
400	4.0	0.0822
800	4.0	0.0008
1600	4.0	0.0234

Temperature 283 K

n	t_{echo} / ms	Intensity
4	0.8	2.0719
8	0.8	2.143
16	0.8	2.0906
36	0.8	2.0916
72	0.8	1.9603
148	0.8	1.778
292	0.8	1.4792
584	0.8	1.0137
1172	0.8	0.47864

Temperature 293 K

n	t_{echo} / ms	Intensity
4	0.8	1.6328
40	0.8	1.6255
88	0.8	1.6246
176	0.8	1.454
352	0.8	1.2774
704	0.8	0.95174
1408	0.8	0.5706
5624	0.8	0.22134
5624	0.8	0.060176

Temperature 303 K

n	t_{echo} / ms	Intensity
4	0.2	3.3742
32	0.2	3.1536
60	0.2	3.2098
120	0.2	3.254
240	0.2	3.1212
600	0.2	3.0278
1000	0.2	2.8759
2000	0.2	2.5498
4000	0.2	2.0468
8000	0.2	1.3012

n	t_{echo} / ms	Intensity
4	0.8	3.2832
8	0.8	3.2339
16	0.8	3.2942
32	0.8	3.3086
60	0.8	3.2933
120	0.8	3.1437
240	0.8	2.9754
600	0.8	2.6756
1000	0.8	2.1247
2000	0.8	1.3898

Temperature 313 K

n	t_{echo} / ms	Intensity
60	1.6256	2.0110
80	1.2089	2.0170
120	0.79223	2.0574
156	0.59993	1.9147
224	0.40533	2.0687
400	0.2089	1.9837

n	t_{echo} / ms	Intensity
4	0.8	1.7416
40	0.8	1.7516
80	0.8	1.6699
240	0.8	1.6762
600	0.8	1.4682
960	0.8	0.9668
1920	0.8	0.5598
4000	0.8	0.1622

Table 5: The *ab initio* calculated *xyz*-coordinates of thiacalix[4]arene.

C	2.578907	3.405005	1.125016
C	0.338850	4.278327	1.108016
C	0.988214	2.603047	-0.522984
C	0.010602	3.460672	0.023016
O	1.834131	-0.644140	-1.584984
C	4.278327	-0.338850	1.108016
C	3.405005	-2.578907	1.125016
C	2.603047	-0.988214	-0.522984
C	3.460672	-0.010602	0.023016
C	4.250850	-1.614496	1.667016
C	2.578907	-2.283806	0.035016
S	1.617968	-3.599209	-0.734984
C	-0.988214	-2.603047	-0.522984
C	-2.578907	-3.405005	1.125016
C	-1.614496	-4.250850	1.667016
C	-0.010602	-3.460672	0.023016
O	-0.644140	-1.834131	-1.584984
C	-0.338850	-4.278327	1.108016
C	-4.278327	0.338850	1.108016
C	-3.460672	0.010602	0.023016
C	1.614496	4.250850	1.667016
O	0.644140	1.834131	-1.584984
S	3.599209	1.617968	-0.734984
C	2.283806	2.578907	0.035016
C	-3.405005	2.578907	1.125016
S	-3.599209	-1.617968	-0.734984
S	-1.617968	3.599209	-0.734984
O	-1.834131	0.644140	-1.584984
C	-2.283806	-2.578907	0.035016
C	-2.578907	2.283806	0.035016
C	-4.250850	1.614496	1.667016
C	-2.603047	0.988214	-0.522984
H	3.584439	3.381970	1.534016
H	-0.422450	4.941575	1.506016
H	1.111070	-1.298435	-1.720984
H	4.941575	0.422450	1.506016
H	3.381970	-3.584439	1.534016
H	4.890046	-1.857744	2.510016
H	-3.584439	-3.381970	1.534016
H	-1.857744	-4.890046	2.510016
H	-1.298435	-1.111070	-1.720984
H	0.422450	-4.941575	1.506016
H	-4.941575	-0.422450	1.506016
H	1.857744	4.890046	2.510016
H	1.298435	1.111070	-1.720984
H	-3.381970	3.584439	1.534016
H	-1.111070	1.298435	-1.720984
H	-4.890046	1.857744	2.510016