Supporting Information for

Distortional Binding of Transition State Analogues to Human PNP probed by MAS Solid State NMR

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1. Data from NMR experiments for inter-nuclear distance measurements

S1/S0 is the REDOR dephasing curve
I1Z and I2Z are the signal intensities of the aromatic and aliphatic carbon atoms, respectively, in the R^2 experiment.
Aro = aromatic carbon
Ali = aliphatic carbon
Exp = experimental values
Sim = simulated

(a) Immucillin-H

Page #1 - "ImmHPNPREDOR2.71" Wednesday, January 16 6:40 PM 2013

	time, ms	S0, aro	S1, aro	S1/S0, aro	S1/S0,sim
0	0.087000	1.5801e+06	1.6116e+06	1.0199	0.99983
1	0.26300	1.5578e+06	1.5519e+06	0.99621	0.99839
2	0.43900	1.5300e+06	1.4830e+06	0.96928	0.99554
3	0.61500	1.5050e+06	1.4681e+06	0.97551	0.99121
4	0.79100	1.4579e+06	1.4595e+06	1.0011	0.98550
5	0.96700	1.4216e+06	1.3824e+06	0.97242	0.97834
6	1.1430	1.3923e+06	1.3480e+06	0.96813	0.96983
7	1.3190	1.3663e+06	1.2777e+06	0.93511	0.95994
8	1.4950	1.3164e+06	1.2308e+06	0.93497	0.94874
9	1.6710	1.2878e+06	1.1722e+06	0.91028	0.93623
10	1.8470	1.2446e+06	1.1317e+06	0.90933	0.92248
11	2.0230	1.2055e+06	1.0553e+06	0.87543	0.90750
12	2.1990	1.1661e+06	1.0393e+06	0.89125	0.89138
13	2.3750	1.1465e+06	9.9659e+05	0.86926	0.87411
14	2.5510	1.1102e+06	9.2944e+05	0.83718	0.85581
15	2.7270	1.0324e+06	8.6589e+05	0.83873	0.83647
16	2.9030	1.0468e+06	8.2239e+05	0.78562	0.81622
17	3.0790	9.9910e+05	7.9438e+05	0.79509	0.79504
18	3.2550	9.3898e+05	7.3303e+05	0.78067	0.77307
19	3.4310	9.1602e+05	6.7041e+05	0.73187	0.75030
20	3.6070	8.3220e+05	6.3164e+05	0.75900	0.72688
21	3.7830	8.3582e+05	5.7284e+05	0.68536	0.70280
22	3.9590	7.9840e+05	5.5141e+05	0.69064	0.67821
23	4.1350	7.4808e+05	5.1691e+05	0.69099	0.65310

fit = 1.0048-0.0122*x-0.017891*x^ 2

	time, ms	S0, aro	S1, aro	aro S1/S0	aro, sim
0	0.087000	8.8544e+09	9.0392e+09	1.0209	0.99983
1	0.26100	8.8581e+09	8.9311e+09	1.0082	0.99843
2	0.43500	8.6840e+09	8.7322e+09	1.0055	0.99562
3	0.60900	8.6908e+09	8.6811e+09	0.99888	0.99137
4	0.78300	8.5831e+09	8.6641e+09	1.0094	0.98574
5	0.95700	8.6213e+09	8.4547e+09	0.98067	0.97869
6	1.1310	8.4633e+09	8.0623e+09	0.95262	0.97030
7	1.3050	8.2869e+09	7.9799e+09	0.96295	0.96053
8	1.4790	8.0267e+09	7.7201e+09	0.96180	0.94949
9	1.6530	8.1286e+09	7.5573e+09	0.92972	0.93714
10	1.8270	8.0264e+09	7.4238e+09	0.92492	0.92357
11	2.0010	7.9641e+09	7.1545e+09	0.89835	0.90878
12	2.1750	7.7240e+09	7.0264e+09	0.90969	0.89286
13	2.3490	7.5618e+09	6.5536e+09	0.86667	0.87580
14	2.5230	7.3939e+09	6.2478e+09	0.84500	0.85771
15	2.6970	7.3185e+09	5.9902e+09	0.81850	0.83860
16	2.8710	7.0672e+09	5.7576e+09	0.81470	0.81857
17	3.0450	6.9180e+09	5.3610e+09	0.77493	0.79763
18	3.2190	6.7961e+09	5.2532e+09	0.77297	0.77589
19	3.3930	6.8022e+09	4.9309e+09	0.72490	0.75337
20	3.5670	6.6398e+09	4.6015e+09	0.69302	0.73018
21	3.7410	6.4273e+09	4.4580e+09	0.69360	0.70634
22	3.9150	6.2090e+09	4.1640e+09	0.67063	0.68197
23	4.0890	6.0672e+09	3.9282e+09	0.64744	0.65709
24	4.2630	5.9043e+09	3.6665e+09	0.62098	0.63183
25	4.4370	5.7276e+09	3.3809e+09	0.59029	0.60620
26	4.6110	5.5832e+09	3.2886e+09	0.58902	0.58032
27	4.7850	5.4246e+09	3.0581e+09	0.56376	0.55422
28	4.9590	5.1673e+09	2.8292e+09	0.54753	0.52802
29	5.1330	4.9536e+09	2.6169e+09	0.52828	0.50174
30	5.3070	4.8325e+09	2.5340e+09	0.52437	0.47551

fit = 1.01-0.0244*x-0.014885*x^ 2

	t, ms	PNP R2, Aro	PNP R2, Ali	PNP Aro-Ali	sim, Aro-Ali
0	0.0000	-1.0103e+10	1.1472e+10	1.0000	0.84097
1	0.11500	-8.5763e+09	1.0011e+10	0.86151	0.80572
2	0.23000	-5.7922e+09	7.9358e+09	0.63630	0.70672
3	0.34500	-5.0928e+09	5.5384e+09	0.49276	0.56277
4	0.46000	-3.4179e+09	4.4815e+09	0.36614	0.40080
5	0.57500	-1.8182e+09	3.0614e+09	0.22617	0.25023
6	0.69000	-1.2639e+09	2.2135e+09	0.16118	0.13701
7	0.80500	-7.0255e+08	1.5653e+09	0.10511	0.078366
8	0.92000	-9.5096e+08	2.1336e+09	0.14297	0.079692
9	1.0350	-1.2937e+09	2.6526e+09	0.18291	0.13393
10	1.1500	-1.7256e+09	3.7161e+09	0.25222	0.22370
11	1.2650	-2.2177e+09	4.3059e+09	0.30237	0.32552
12	1.3800	-2.9292e+09	4.6049e+09	0.34920	0.41521
13	1.4950	-3.1867e+09	5.2227e+09	0.38977	0.47316
14	1.6100	-3.6767e+09	5.8043e+09	0.43944	0.48838
15	1.7250	-3.9403e+09	5.7498e+09	0.44914	0.46043
16	1.8400	-3.8727e+09	5.2726e+09	0.42389	0.39886

fit = 0.84-0.087*x-1.66*x^ 2-4.52*x^ 3+12.75*x^ 4-10.14*x^ 5+3.32*x^ 6-0.39*x^ 7

	time, ms	exp, Aro	exp, Ali	exp Ali-Aro	sim, ali-aro
0	0.0000	-1.0586e+10	1.4003e+10	1.0000	0.80638
1	0.10500	-9.1981e+09	1.1413e+10	0.83823	0.76014
2	0.21000	-6.5858e+09	8.4952e+09	0.61332	0.63179
3	0.31500	-3.3842e+09	6.0810e+09	0.38494	0.44987
4	0.42000	-5.9996e+08	3.4101e+09	0.16309	0.25406
5	0.52500	-3.4457e+09	1.3870e+09	0.19654	0.085586
6	0.63000	5.5129e+08	1.0866e+09	0.021769	-0.022683
7	0.73500	1.4241e+08	1.3878e+09	0.050649	-0.053715
8	0.84000	-1.7175e+08	1.9314e+09	0.085533	-0.0096937
9	0.94500	-2.4350e+08	3.3074e+09	0.14441	0.089531
10	1.0500	-9.8703e+08	4.7677e+09	0.23404	0.21235
11	1.1550	-2.0202e+09	5.5433e+09	0.30760	0.32399
12	1.2600	-2.8261e+09	5.6635e+09	0.34526	0.39555
13	1.3650	-3.0618e+09	5.6345e+09	0.35367	0.41099
14	1.4700	-2.3196e+09	5.0565e+09	0.29998	0.37051
15	1.5750	-1.5949e+09	4.4287e+09	0.24497	0.28942
16	1.6800	-5.0960e+08	3.2990e+09	0.15489	0.19310
17	1.7850	-3.2499e+06	1.9969e+09	0.081342	0.10952
18	1.8900	-2.1554e+07	1.7369e+09	0.071515	0.061484
19	1.9950	-1.1359e+08	1.7596e+09	0.076181	0.060641
20	2.1000	-2.9479e+07	2.1683e+09	0.089381	0.10483
21	2.2050	-3.1253e+08	2.7873e+09	0.12607	0.17937
22	2.3100	-9.4477e+08	3.5479e+09	0.18271	0.26177
23	2.4150	-1.9329e+09	4.5102e+09	0.26203	0.32837
24	2.5200	-3.0212e+09	4.9955e+09	0.32603	0.36101

fit = 0.78436+1.44*x-14.644*x^ 2+25.542*x^ 3-17.127*x^ 4+4.166*x^ 5+0.13177*x^ 6-0.13379*x^ 7

(b) DADMe-Immucillin-H

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	A	S0 aro	S1 aro	S1/S0 aro	sim S1/S0, aro
0	0.067000	3.8099e+05	3.9142e+05	1.0274	0.99990
1	0.20100	3.6635e+05	3.9294e+05	1.0726	0.99903
2	0.33500	3.5615e+05	3.6448e+05	1.0234	0.99729
3	0.46900	3.3769e+05	3.5146e+05	1.0408	0.99462
4	0.60300	3.2735e+05	3.5104e+05	1.0724	0.99109
5	0.73700	3.4113e+05	3.4517e+05	1.0118	0.98666
6	0.87100	3.4417e+05	3.4072e+05	0.99000	0.98138
7	1.0050	3.4540e+05	3.5171e+05	1.0183	0.97521
8	1.1390	3.3014e+05	3.3280e+05	1.0081	0.96821
9	1.2730	3.1849e+05	3.1420e+05	0.98651	0.96034
10	1.4070	3.0330e+05	3.0659e+05	1.0109	0.95168
11	1.5410	2.9502e+05	2.8387e+05	0.96218	0.94219
12	1.6750	2.8523e+05	2.7096e+05	0.94997	0.93193
13	1.8090	2.7459e+05	2.5724e+05	0.93680	0.92088
14	1.9430	2.8273e+05	2.5921e+05	0.91679	0.90911
15	2.0770	2.8015e+05	2.5217e+05	0.90011	0.89659
16	2.2110	2.7102e+05	2.4917e+05	0.91937	0.88338
17	2.3450	2.5366e+05	2.2846e+05	0.90065	0.86949
18	2.4790	2.4906e+05	2.1035e+05	0.84456	0.85495
19	2.6130	2.4179e+05	2.1200e+05	0.87681	0.83978
20	2.7470	2.3751e+05	1.9257e+05	0.81081	0.82403
21	2.8810	2.2919e+05	1.7598e+05	0.76782	0.80770
22	3.0150	2.0815e+05	1.6879e+05	0.81089	0.79085
23	3.1490	2.1155e+05	1.5978e+05	0.75527	0.77348
24	3.2830	1.9524e+05	1.4583e+05	0.74694	0.75566
25	3.4170	1.8786e+05	1.3038e+05	0.69403	0.73738
26	3.5510	1.7068e+05	1.3087e+05	0.76672	0.71871
27	3.6850	1.7690e+05	1.2850e+05	0.72637	0.69966
28	3.8190	1.7034e+05	1.0232e+05	0.60066	0.68028

fit = 1.004-0.0107*x-0.01966*x^ 2

	time, ms	aro, S0	aro, S1	aro, S1/S0	sim, S1/S0
0	0.067000	9.7298e+09	9.5899e+09	0.98562	0.99993
1	0.20100	9.5906e+09	9.4062e+09	0.98077	0.99936
2	0.33500	9.4228e+09	9.4474e+09	1.0026	0.99821
3	0.46900	9.3844e+09	9.3258e+09	0.99375	0.99646
4	0.60300	9.4747e+09	9.1547e+09	0.96623	0.99413
5	0.73700	9.2054e+09	9.1921e+09	0.99856	0.99120
6	0.87100	9.4808e+09	9.3408e+09	0.98524	0.98770
7	1.0050	9.4363e+09	8.9594e+09	0.94946	0.98360
8	1.1390	9.1337e+09	9.4405e+09	1.0336	0.97895
9	1.2730	8.9809e+09	8.8392e+09	0.98422	0.97371
10	1.4070	9.0313e+09	8.6514e+09	0.95794	0.96794
11	1.5410	8.8089e+09	8.6109e+09	0.97753	0.96158
12	1.6750	8.5218e+09	8.4827e+09	0.99542	0.95471
13	1.8090	8.5651e+09	8.5102e+09	0.99359	0.94727
14	1.9430	8.4234e+09	7.7508e+09	0.92015	0.93933
15	2.0770	8.5112e+09	8.0354e+09	0.94410	0.93085
16	2.2110	8.3831e+09	7.5668e+09	0.90263	0.92189
17	2.3450	8.2066e+09	7.5168e+09	0.91595	0.91241
18	2.4790	7.9647e+09	7.0978e+09	0.89116	0.90246
19	2.6130	7.8316e+09	6.9455e+09	0.88685	0.89203
20	2.7470	7.6908e+09	6.7435e+09	0.87682	0.88116
21	2.8810	7.6400e+09	6.7629e+09	0.88520	0.86982
22	3.0150	7.6472e+09	6.4100e+09	0.83822	0.85807
23	3.1490	7.4580e+09	6.4236e+09	0.86131	0.84589
24	3.2830	7.4576e+09	5.9813e+09	0.80204	0.83333
25	3.4170	7.4370e+09	6.1496e+09	0.82689	0.82036
26	3.5510	7.1242e+09	5.6239e+09	0.78941	0.80705
27	3.6850	6.8401e+09	5.5234e+09	0.80751	0.79336
28	3.8190	6.7661e+09	5.4822e+09	0.81024	0.77935
29	3.9530	6.7527e+09	5.0249e+09	0.74413	0.76501
30	4.0870	6.5546e+09	4.8993e+09	0.74746	0.75039

fit = 1.0023-0.0057686*x-0.0138*x^ 2

	time, ms	ali	aro	ali-aro, exp	ali-aro, sim
0	0.0000	1.2400e+10	-1.5525e+10	0.99999	0.87208
1	0.090900	9.7491e+09	-1.4369e+10	0.86365	0.83584
2	0.18180	6.6981e+09	-1.2307e+10	0.68055	0.73420
3	0.27270	4.9076e+09	-5.5597e+09	0.37482	0.58687
4	0.36360	2.1353e+09	-5.3701e+09	0.26876	0.42195
5	0.45450	1.1071e+09	-3.8504e+09	0.17752	0.27001
6	0.54540	-5.9571e+07	-4.3318e+09	0.15298	0.15767
7	0.63630	3.0037e+08	-1.9262e+09	0.079730	0.10217
8	0.72720	1.0337e+09	-3.6609e+09	0.16811	0.10822
9	0.81810	2.1420e+09	-3.8301e+09	0.21386	0.16752
10	0.90900	4.0414e+09	-5.9261e+09	0.35693	0.26123
11	0.99990	5.1198e+09	-6.6899e+09	0.42289	0.36464
12	1.0908	6.1109e+09	-8.2207e+09	0.51320	0.45288
13	1.1817	6.7140e+09	-9.3790e+09	0.57627	0.50650
14	1.2726	6.6888e+09	-8.5884e+09	0.54706	0.51547
15	1.3635	5.4217e+09	-9.1799e+09	0.52287	0.48091
16	1.4544	5.3051e+09	-7.6369e+09	0.46344	0.41415
17	1.5453	3.4233e+09	-6.6203e+09	0.35965	0.33349
18	1.6362	2.2457e+09	-6.3897e+09	0.30923	0.25951
19	1.7271	1.0367e+09	-6.0528e+09	0.25387	0.21001
20	1.8180	7.2981e+08	-4.2467e+09	0.17820	0.19594
21	1.9089	1.3967e+09	-5.4442e+09	0.24497	0.21904
22	1.9998	1.2325e+09	-4.4130e+09	0.20216	0.27192

fit = 0.869+0.148*x-5.08*x^ 2-1.956*x^ 3+23*x^ 4-26.52*x^ 5+11.74*x^ 6-1.842*x^ 7

	time, ms	exp, aro	sim, aro
0	0.0000	1.00000	0.80703
1	0.095000	0.80268	0.77244
2	0.19000	0.52867	0.67593
3	0.28500	0.33957	0.53763
4	0.38000	0.18859	0.38589
5	0.47500	0.15072	0.25080
6	0.57000	0.11372	0.15747
7	0.66500	0.10602	0.12054
8	0.76000	0.20443	0.14140
9	0.85500	0.30198	0.20850
10	0.95000	0.38222	0.30069
11	1.0450	0.44660	0.39279
12	1.1400	0.49008	0.46173
13	1.2350	0.52591	0.49196
14	1.3300	0.50104	0.47878
15	1.4250	0.42247	0.42878
16	1.5200	0.36715	0.35753
17	1.6150	0.31078	0.28508
18	1.7100	0.29165	0.23061
19	1.8050	0.23660	0.20756
20	1.9000	0.21421	0.22044
21	1.9950	0.23358	0.26410
22	2.0900	0.28913	0.32553
23	2.1850	0.33209	0.38763
24	2.2800	0.37897	0.43389
25	2.3750	0.43389	0.45271
26	2.4700	0.45470	0.44029
27	2.5650	0.47293	0.40133
28	2.6600	0.44636	0.34746

fit = 0.869+0.148*x-5.08*x^ 2-1.956*x^ 3+23*x^ 4-26.52*x^ 5+11.74*x^ 6-1.842*x^ 7

2. Error analysis

Compound	Distance, A	Correlation coefficient (student t fit in Kaleidograph)	Distance variance, A
ImmH C-C	1.47	0.95338	0.07
ImmH C-N	2.72	0.99418	0.02
ImmH-PNP C-C	1.57	0.96649	0.05
ImmH-PNP C-N	2.71	0.98604	0.04
DADMe-ImmH C-C	1.45	0.8952	0.15
DADMe-ImmH C-N	2.87	0.96352	0.1
DADMe-PNP C-C	1.44	0.9322	0.1
DADMe-PNP C-N	2.69	0.9763	0.06

3. Coordinates of calculated fixed distance geometries

Imm-H C-C fixed at 1.47 B3LYP/6-31+G**

O	1.444984	2.704795	1.537080
C	2.267923	2.156107	0.516602
C	2.557662	0.725333	0.945526
N	1.236303	0.016636	1.274009
C	3.237198	-0.169578	-0.102683
O	4.229531	-0.912503	0.575542
C	2.116415	-1.103275	-0.617970
O	2.658692	-2.308234	-1.111894
C	1.265627	-1.375992	0.648479
C	-0.097530	-1.890549	0.453718
C	-0.543167	-3.205546	0.509037
N	-1.874487	-3.242689	0.195925
C	-2.318108	-1.969260	-0.049226
C	-3.632566	-1.495404	-0.389638
O	-4.659487	-2.132084	-0.556384
N	-3.595093	-0.076173	-0.520059
C	-2.499041	0.717096	-0.337216
N	-1.311358	0.268581	-0.034828
C	-1.235765	-1.104582	0.100010
H	1.760222	2.178143	-0.459810
H	3.223960	2.685575	0.421645
H	3.155491	0.724507	1.858625
H	0.421975	0.535956	0.875538
H	3.671919	0.425246	-0.917691
H	1.506120	-0.591221	-1.372230
H	2.381977	-2.469075	-2.022424
H	1.863331	-2.016630	1.303007
H	0.001083	-4.111013	0.736740
H	-2.658343	1.784515	-0.456310
H	1.078170	-0.019980	2.283025
H	4.533714	-1.626954	-0.006873
H	1.302821	3.649497	1.391493
H	-2.456199	-4.069679	0.164450
H	-4.484855	0.352484	-0.756053

Calculated Atom-atom overlap-weighted NAO bond order = 0.9227

Imm-H C-C fixed at 1.57 B3LYP/6-31+G**

O	1.235289	1.042273	3.335489

C	2.224454	1.140840	2.320133
C	2.430117	-0.276193	1.806505
N	1.068287	-0.885386	1.434134
C	3.287463	-0.420168	0.539880
O	4.137924	-1.529376	0.745736
C	2.276930	-0.713627	-0.596652
O	2.902194	-1.422955	-1.643473
C	1.212952	-1.589037	0.096759
C	-0.189007	-1.685761	-0.603280
C	-0.656909	-2.647848	-1.485645
N	-1.920628	-2.302186	-1.885960
C	-2.288433	-1.133953	-1.271016
C	-3.516033	-0.389470	-1.353435
O	-4.515383	-0.625343	-2.011779
N	-3.424195	0.753293	-0.505423
C	-2.356019	1.089154	0.275830
N	-1.246775	0.404360	0.334681
C	-1.227622	-0.722613	-0.464882
H	1.898606	1.810403	1.509445
H	3.183867	1.506867	2.706178
H	2.851800	-0.899708	2.596808
H	0.333229	-0.145378	1.345471
H	3.863983	0.493052	0.338299
H	1.820797	0.218681	-0.951549
H	2.768803	-0.982777	-2.492003
H	1.641331	-2.577933	0.272864
H	-0.179710	-3.543293	-1.856842
H	-2.467991	1.987389	0.875425
H	0.736769	-1.517139	2.165862
H	4.539897	-1.773040	-0.103546
H	1.127909	1.887031	3.792311
H	-2.506166	-2.822994	-2.525672
H	-4.251875	1.341402	-0.494376

Calculated Atom-atom overlap-weighted NAO bond order = 0.8586

Loss of bond order upon 0.1 Å bond stretch = 0.0641
Energy associated with loss of bond order = 0.0641 * average C-C bond energy = 0.0641*85 kcal/mol = 5.5 kcal/mol