Supporting Information
Computation of deuterium isotope perturbation of ^{13}C NMR chemical shifts of alkanes: a local mode zero point level approach

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Figure S1. Correlation of the calculated and observed deuterium induced ^{13}C chemical shifts for the individual deuterium isotopomers of adamantane. Any difference in the slope of the lines for these correlations would indicate that the values of one or more of the four stretch and bend parameters of the distribution functions for one of the CD bonds differed from those of the other. Concurrence of the lines indicates that the assumption that the parameters for both bonds are the same is justified. In this case the values for both CH bonds appear to be the same and result in values that are uniformly ca. 9% too high. A more detailed analysis with a fit of a and b in the form y = a + bx yields values for the constants $a_{(C1D)}$ and $a_{(C2D)}$ of -8.5 (14) and 1.09 (1.4) where the quantities in parentheses are the standard deviations of the value. These are thus both zero within one standard deviation. The values of the sloes $b_{(C1D)}$ and $b_{(C2D)}$ are 1.12 (0.06) and 1.086 (0.017). These are the same to within one standard deviation.

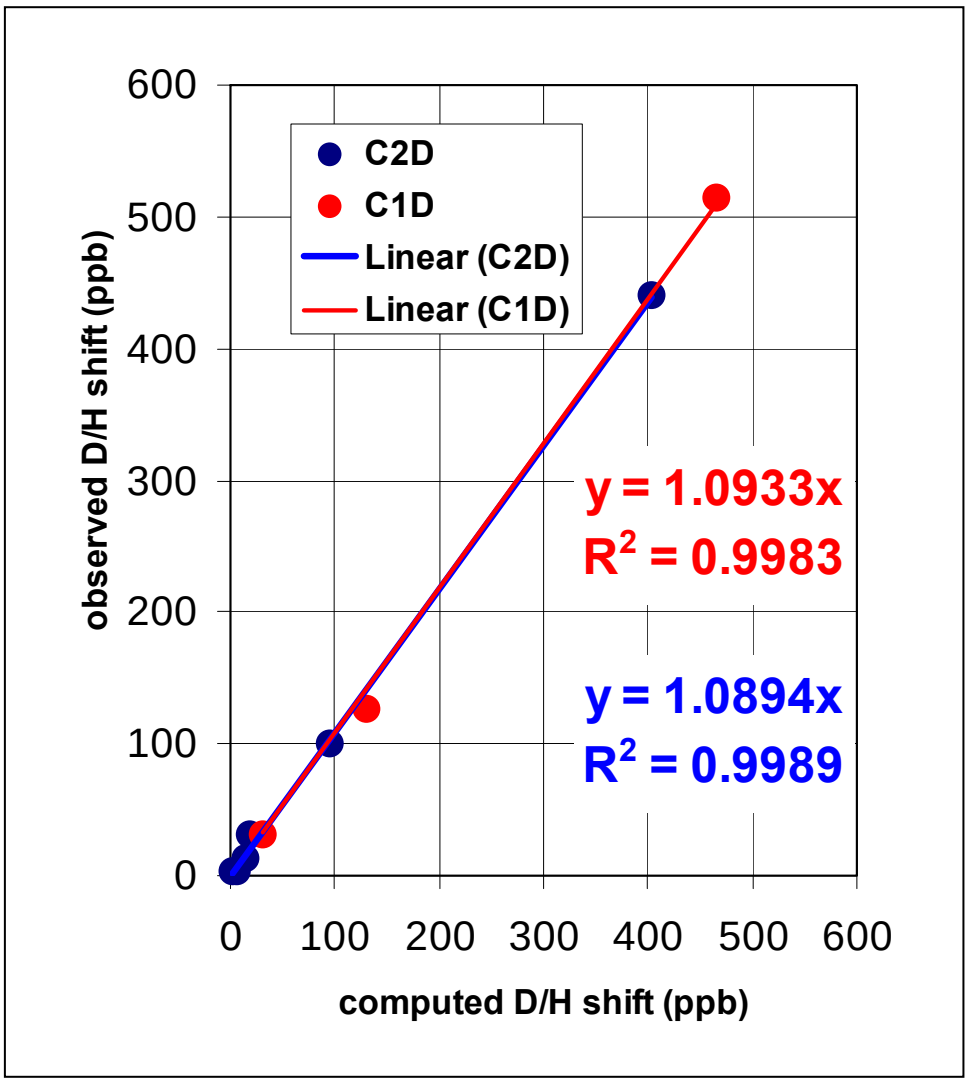


Table S1. Calculated and observed deuterium induced ^{13}C chemical shifts for protoadamantane arranged by specific monodeutero species. The label comes from Fig. 1. n represents the number of bonds between the D and ^{13}C atoms.

label	calc.	obs.	diff.	n
1a	86.8	90.0	-3.2	2
1a	355.6	376.0	-20.4	1
1a	93.8	105.0	-11.2	2
1a	13.3	20.0	-6.7	3
1a	9.2	15.0	-5.8	3
1b	91.6	90.0	1.6	2
1b	359.8	407.0	-47.2	1
1b	81.0	83.0	-2.0	2
1b	44.6	52.0	-7.4	3
1b	-24.0	-6.0	-18.0	4
1b	1.3	5.0	-3.7	4
1b	11.3	14.0	-2.7	4
1b	4.5	7.0	-2.5	3
1b	22.1	27.0	-4.9	3
2a	18.0	31.0	-13.0	3
2a	83.6	101.0	-17.4	2
2a	357.0	374.0	-17.0	1
2a	72.9	78.0	-5.1	2
2b	30.5	24.0	6.5	3
2b	86.7	95.0	-8.3	2
2b	397.0	417.0	-20.0	1
2b	107.0	109.0	-2.0	2
2b	20.2	23.0	-2.8	3
2b	-4.4	-14.0	9.6	4
2b	24.8	37.0	-12.2	3

label	calc.	obs.	diff.	n
3a	-4.6	-12.0	7.4	4
3a	22.5	20.0	2.5	3
3a	97.0	98.0	-1.0	2
3a	370.9	392.0	-21.1	1
3a	90.3	90.0	0.3	2
3a	6.9	12.0	-5.1	3
3b	-31.3	-17	-14.3	4
3b	1.1	8.0	-6.9	3
3b	89.7	95.0	-5.3	2
3b	384.1	417.0	-32.9	1
3b	88.8	107.0	-18.2	2
3b	18.0	31.0	-13.0	3
3b	63.9	55.0	8.9	3
4a	84.8	89.0	-4.2	2
4a	23.4	29.0	-5.6	3
4a	-10.2	-8.0	-2.2	4
4a	21.9	31.0	-9.1	3
4a	86.4	91.0	-4.6	2
4a	17.4	15.0	2.4	3
4a	393.6	421.0	-27.4	1
4b	102.1	104.0	-1.9	2
4b	20.4	25.0	-4.6	3
4b	5.2	5.0	0.2	4
4b	47.6	50.0	-2.4	3
4b	90.4	104.0	-13.6	2
4b	25.6	34.0	-8.4	3
4b	23.0	32.0	-9.0	3
4b	411.0	453.0	-42.0	1

Figure S2. Correlation of the calculated and observed deuterium induced ^{13}C chemical shifts for the individual deuterium isotopomers of protoadamantane for $^{n}\Delta$, n>1. Any difference in the slope of the lines for these correlations would indicate that the values of one or more of the four stretch and bend parameters of the distribution functions for one of the CD bonds differs from those of the others. Concurrence of the lines indicates that the assumption that the parameters for all bonds are the same is justified at least in so far as this data is concerned. The five cases for which there are at least 6 data points are analyzed in Table S1. The values of the slopes for these five cases are in the range from 0.91 to 1.08 with an average of 1.00 with a standard deviation of 0.07. This is smaller than the standard deviations of most of the slopes. This indicates that no enhancement of the deviation of the calculated and observed values is introduced by the assumption that all of the CH bonds have the same geometric H/D changes.

Table S2. Intercept and slope values for the observed and computed ^{13}C H/D chemical shifts of individual isotopomeric forms of protoadamantane. S(k) is the standard deviation of **a** or **b** in y = **a** + **b**x. The number of points in each data set is **n**.

#	n	a	S(a)	b	S(b)
1b	8	7.7	0.96	0.91	0.05
2b	6	-2	3.2	1.08	0.09
3b	6	9.8	3.3	0.96	0.10
4a	6	3.2	1.4	1.02	0.05
4b	7	4.2	5.8	1.03	0.17
			ave:	1.00	

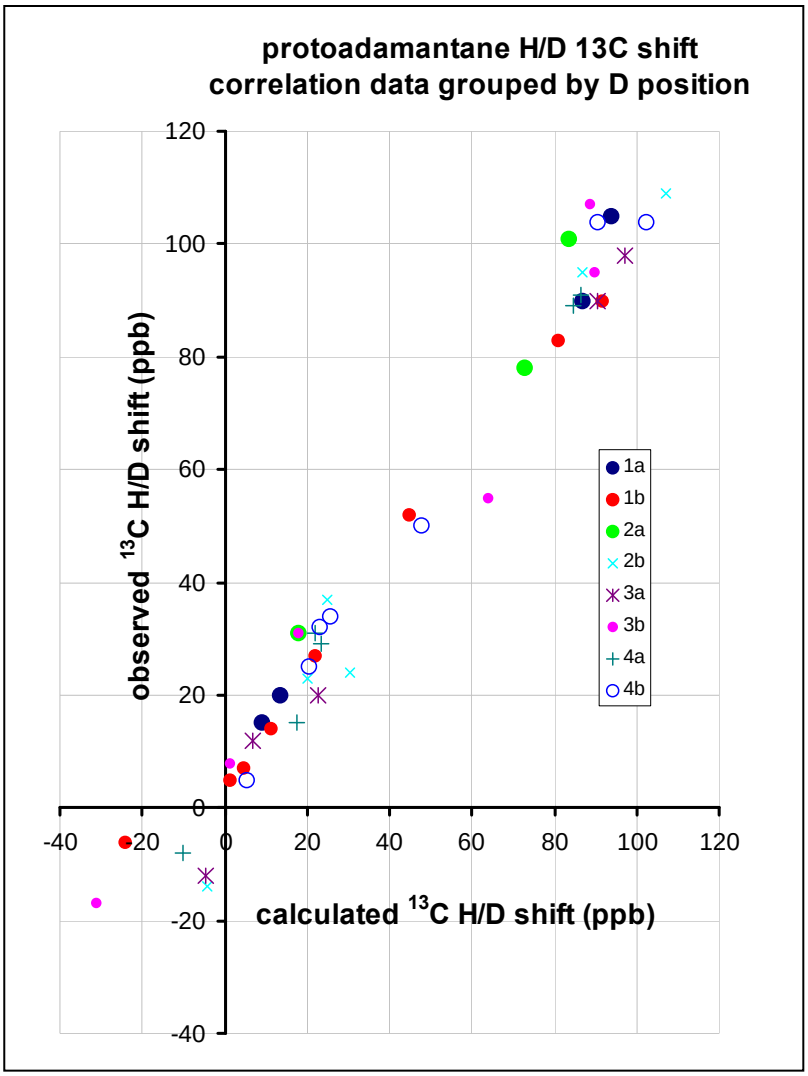


Figure S3 Correlation of all computed and observed deuterium induced chemical shifts for all molecules considered for $^{n}\Delta$ n > 1. The red line is through all data points (including the two outliers); the blue line is through all data points except the two outliers. The slope for the fit to the data minus the two outliers has a slope of 1.033 and a correlation coefficient of 0.97.

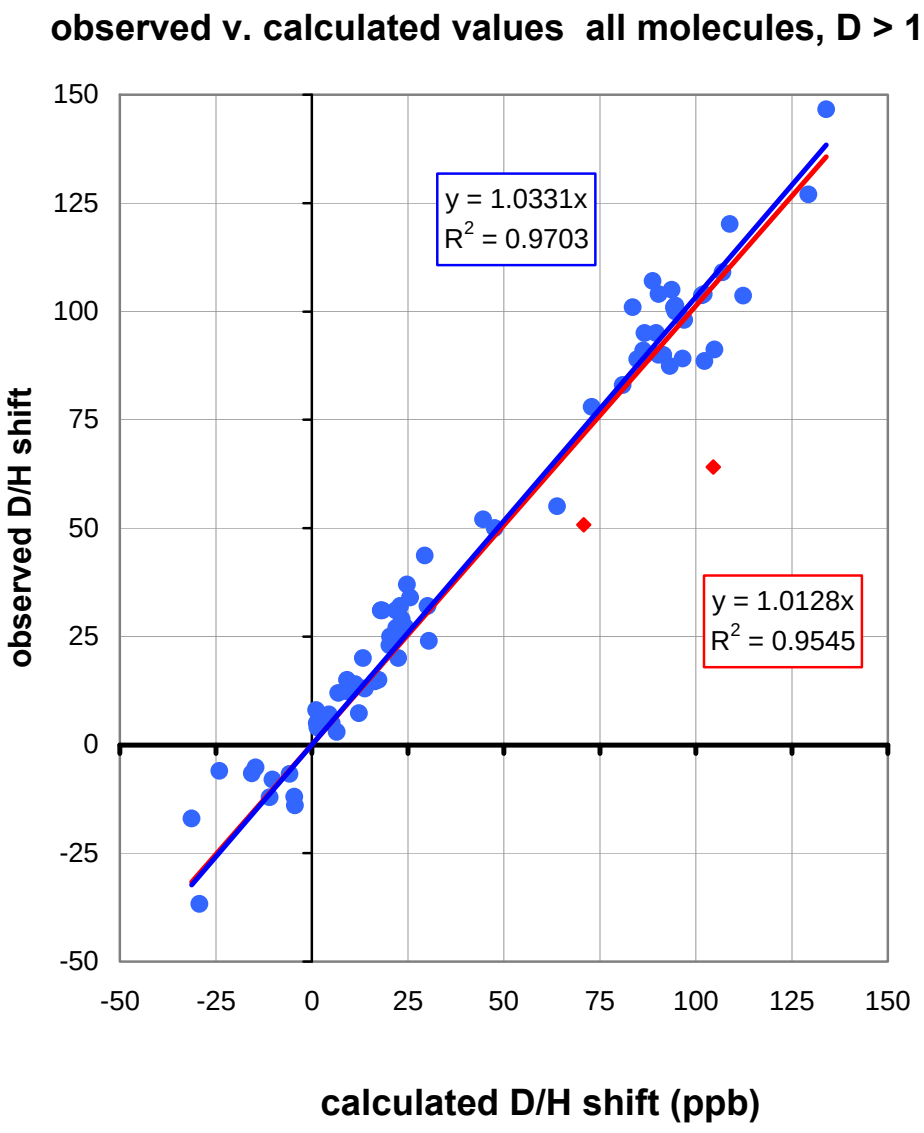
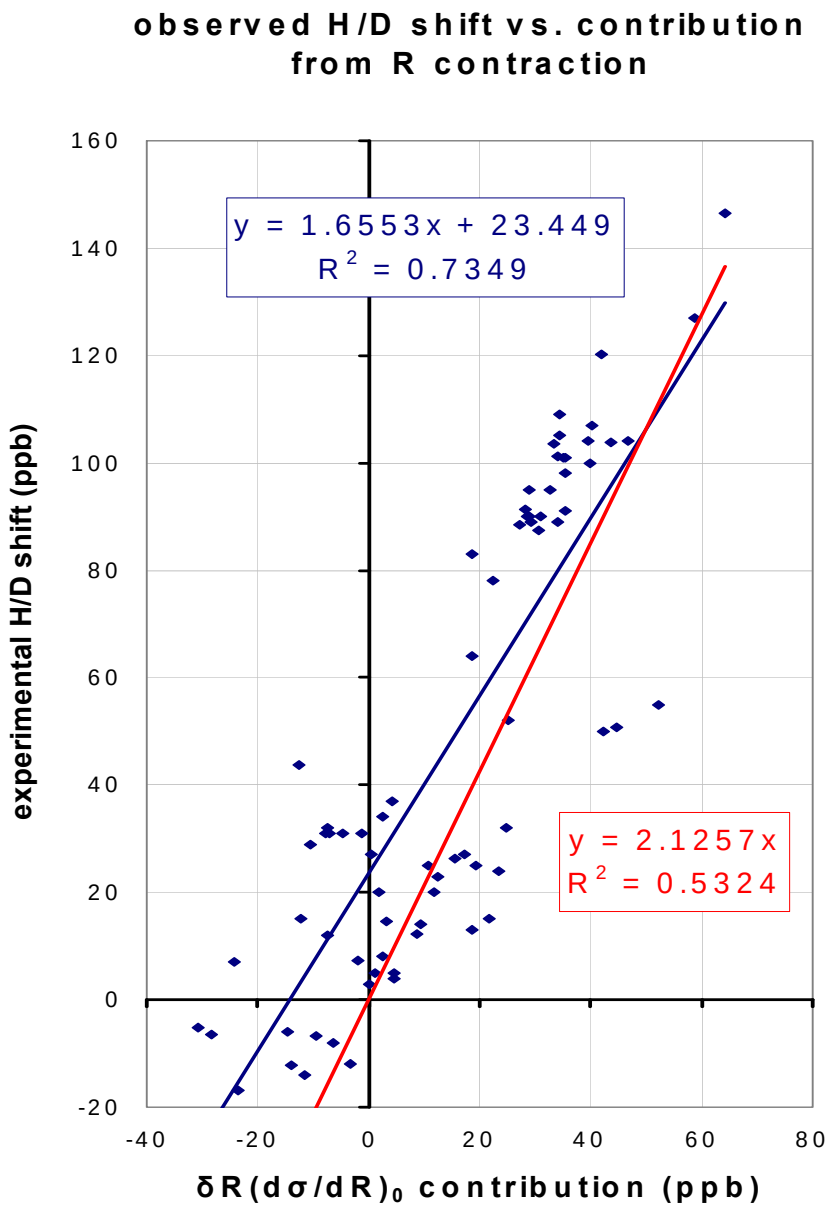


Figure S4. Correlation of the observed H/D chemical shifts with the contribution made by the contraction of the CD bond relative to the CH bond for all $^{n}\Delta$ shifts n > 1. The observed variation is about twice as large as is calculated. The red line is constrained to go through the origin.



Figures S5 & S6:

Correlation of observed and calculated values of $^{1}\Delta$ H/D ^{13}C shifts with just the stretch contribution due to change in bond length and with the full calculation. These are the shifts observed at the carbon which is deuterated. The full treatment includes the effect of change in bond length plus the restriction in the width of the stretch distribution and the two bend contributions.

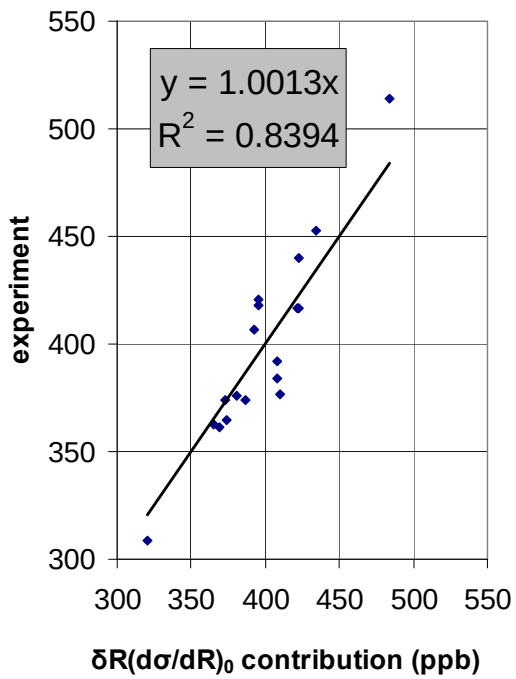


Figure S5. Correlation of observed $^{1}\Delta$ H/D ^{13}C shift values with the contribution due to the change in bond length only.

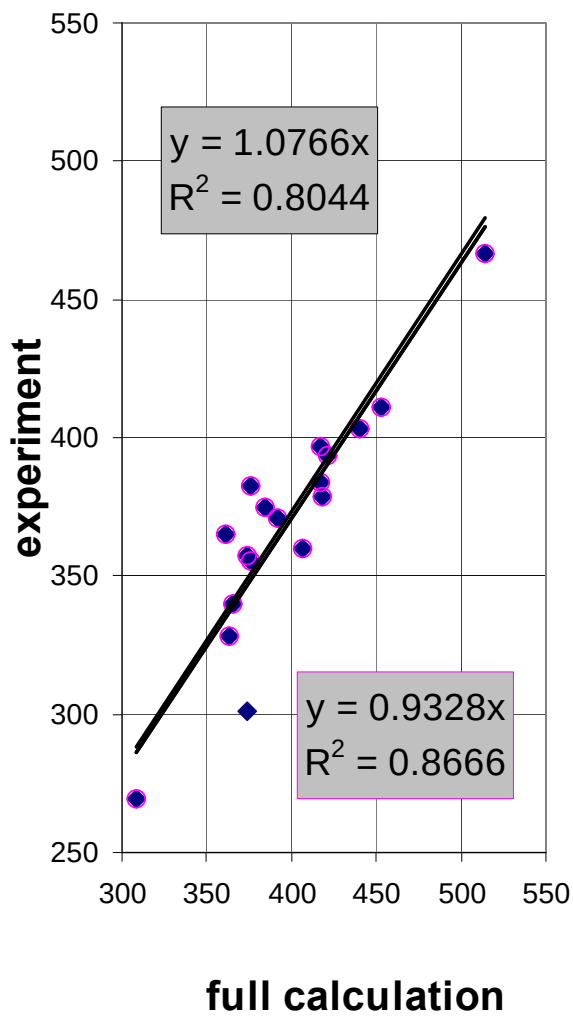


Figure S6. Experimental and calculated $^{1}\Delta$ H/D chemical shifts using full calculation. Fits are for all data and for the case where the cyclopentane value has been removed.