Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A Molecular Mechanical Model for N-Heterocyclic Carbenes

Supporting Information

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1 Bond Stretching and Angle Bending Parameters

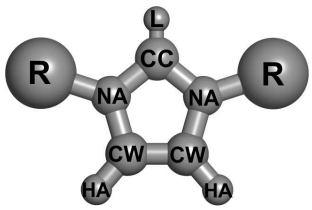

Figure 1: Structure of **1** with the names of the atoms.

Table 1: Bond stretching and angle bending parameters for **1**. The force constants k_l and k_θ are taken from the OPLS/AA force field. The optima l_0 and θ_0 are obtained from an optimization at a HF/6-31(d) level of theory.

bond-/angletype	l_0 / θ_0 Å/ degree	k_l / k_θ kcal mol^{-1} Å^{-2} / kcal mol^{-1} rad^{-1}
CC-L	0.100	rigid
CC-NA	1.352	rigid
CW-NA	1.385	427.5
CW-HA	1.069	385.0
CW-CW	1.333	520.6
CT-NA	1.443	337.0
NA-CC-L	128.75	rigid
NA-CC-NA	102.50	rigid
CW-NA-CC	112.46	70.0
CW-CW-NA	106.28	70.0
CC-NA-CT	123.30	70.0
CW-NA-CT	124.24	70.0
CW-CW-HA	130.78	35.0
NA-CW-HA	122.94	35.0

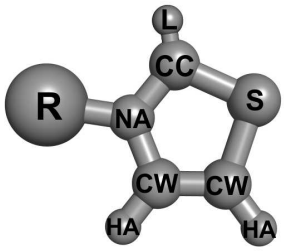

Figure 2: Structure of **2** with the names of the atoms.

Table 2: Bond stretching and angle bending parameters for **2**.

bond-/angletype	l_0 / θ_0 Å/ degree	k_l / k_θ kcal mol^{-1} Å^{-2} / kcal mol^{-1} rad^{-1}
CC-L	0.200	rigid
CC-NA	1.330	rigid
CC-S	1.724	rigid
CW-NA	1.397	427.5
CW-S	1.743	300.0
CW-CW	1.327	520.6
CW-HA	1.071	385.0
NA-CT	1.455	337.0
S-CC-L	136.76	rigid
NA-CC-L	117.37	rigid
S-CC-NA	105.87	rigid
CC-NA-CW	118.50	70.0
CC-NA-CT	121.13	70.0
CC-S-CW	94.34	80.0
S-CW-CW	108.64	70.0
NA-CW-CW	112.64	70.0
NA-CW-HA	119.47	35.0
S-CW-HA	123.93	35.0
CW-NA-CT	120.37	70.0
CW-CW-HA	127.76	35.0

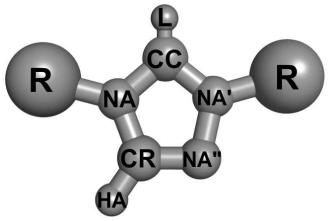

Figure 3: Structure of **3** with the names of the atoms.

Table 3: Bond stretching and angle bending parameters for **3**.

bond-/angletype	l_0 / θ_0 Å/ degree	k_l / k_θ kcal mol^{-1} Å^{-2} / kcal mol^{-1} rad^{-1}
CC-L	0.300	rigid
CC-NA	1.364	rigid
CC-NA'	1.332	rigid
NA-CR	1.364	477.0
NA'-NA"	1.365	400.0
NA"-CR	1.271	477.0
CR-H4	1.070	367.0
NA-CT	1.444	337.0
NA-CC-L	130.44	rigid
NA'-CC-L	128.85	rigid
NA'-CC-NA	100.72	rigid
CC-NA-CR	109.49	70.0
CC-NA'-NA"	115.42	56.0
CC-NA-CT	124.62	70.0
CC-NA'-CT	126.21	70.0
NA'-NA"-CR	103.18	70.0
NA"-NA'-CT	118.37	70.0
CR-NA-CT	125.88	70.0
NA-CR-NA"	111.19	70.0
NA-CR-HA	124.41	35.0

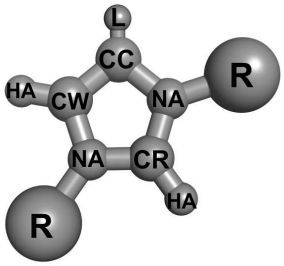

Figure 4: Structure of **4** with the names of the atoms.

Table 4: Bond stretching and angle bending parameters for **4**.

bond-/angletype	l_0 / θ_0 Å/ degree	k_l / k_θ kcal mol^{-1} Å^{-2} / kcal mol^{-1} rad^{-1}
CC-L	0.100	rigid
CC-NA	1.415	rigid
CC-CW	1.367	rigid
NA-CR	1.314	477.0
NA-CW	1.398	427.5
CW-HA	1.070	385.0
CR-HA	1.070	385.0
NA-CT	1.446	337.0
NA-CC-L	131.05	rigid
CW-CC-L	128.66	rigid
CC-NA-CR	112.89	70.0
CC-NA-CT	122.47	70.0
CC-CW-NA	111.44	70.0
CC-CW-HA	129.94	35.0
CW-NA-CR	106.90	70.0
CW-NA-CT	126.64	70.0
CR-NA-CT	125.55	70.0
NA-CR-HA	125.76	35.0

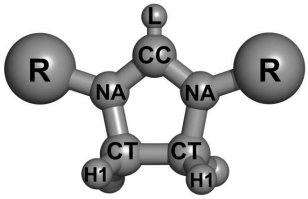

Figure 5: Structure of **5** with the names of the atoms.

Table 5: Bond stretching and angle bending parameters for **5**.

bond-/angletype	l_0 / θ_0 Å/ degree	k_l / k_θ kcal mol^{-1} Å^{-2} / kcal mol^{-1} rad^{-1}
CC-L	0.250	rigid
CC-NA	1.341	rigid
NA-CT	1.436	337.0
NA-CT*	1.455	337.0
CT-CT	1.532	310.0
CT-H1	1.087	331.0
NA-CC-L	127.22	rigid
CC-NA-CT	123.55	70.0
CC-NA-CT*	114.80	70.0
NA-CT-H1	111.18	50.0
CT-CT-H1	112.54	35.0
CT-CT-NA	101.57	50.0
CT-NA-CT	120.62	50.0

*CT in the ring.

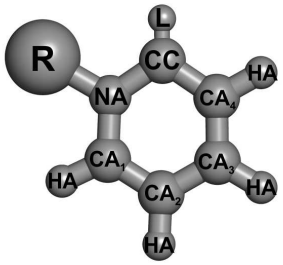

Figure 6: Structure of **6** with the names of the atoms.

Table 6: Bond stretching and angle bending parameters for **6**.

bond-/angletype	l_0 / θ_0 Å/ degree	k_l / k_θ kcal mol^{-1} Å^{-2} / kcal mol^{-1} rad^{-1}
CC-L	0.250	rigid
NA-CC	1.354	rigid
CC-CA4	1.434	rigid
CA3-CA4	1.354	469.0
CA1-CA2	1.354	469.0
CA2-CA3	1.415	469.0
CA1-NA	1.362	483.0
CA-HA	1.075	367.0
NA-CT	1.462	337.0
NA-CC-L	121.42	rigid
CA4-CC-L	126.31	rigid
CA1-NA-CC	125.91	70.0
CA3-CA4-CC	123.81	63.0
CA1-CA2-CA3	118.45	63.0
CA2-CA3-CA4	118.45	63.0
NA-CA1-CA2	121.11	70.0
HA-CA4-CC	116.96	35.0
HA-CA-CA	120.76	35.0
HA-CA1-NA	116.49	35.0
CA1-NA-CT	116.50	70.0
CC-NA-CT	117.60	70.0

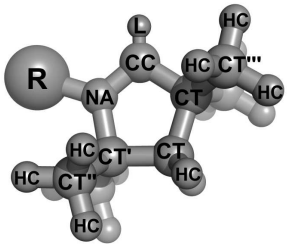

Figure 7: Structure of **7** with the names of the atoms.

Table 7: Bond stretching and angle bending parameters for **7**.

bond-/angletype	l_0 / θ_0 Å/ degree	k_l / k_θ kcal mol^{-1} Å^{-2} / kcal mol^{-1} rad^{-1}
CC-L	0.100	rigid
CC-NA	1.306	rigid
CC-CT	1.521	rigid
NA-CT	1.436	337.0
NA-CT'	1.487	337.0
CT-HC	1.085	331.0
CT-CT	1.545	310.0
CT-CT'	1.545	310.0
CT''-CT'	1.534	310.0
CT'''-CT	1.534	310.0
NA-CC-L	120.9	rigid
CT-CC-L	132.6	rigid
CC-NA-CT	120.9	70.0
CC-NA-CT'	118.9	70.0
CT'-CT-HC	111.1	35.0
HC-CT-HC	106.9	35.0
CT-CT'-NA	101.1	70.0
CT'-NA-CT	120.2	70.0
CT-CT-CC	106.0	63.0
CT'''-CT-CC	108.6	63.0
NA-CT'-CT''	110.9	70.0
CT-CC-NA	106.5	70.0
CT'-CT-CT	105.6	40.0
CT'''-CT-CT'''	109.5	40.0
CT-CT-CT'''	112.1	40.0

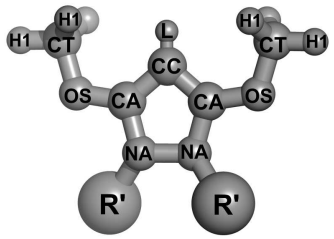

Figure 8: Structure of **8** with the names of the atoms.

Table 8: Bond stretching and angle bending parameters for **8**.

bond-/angletype	l_0 / θ_0 Å/ degree	k_l / k_θ kcal mol^{-1} Å^{-2} / kcal mol^{-1} rad^{-1}
CC-L	0.250	rigid
CC-CA	1.379	rigid
CA-NA	1.374	418.0
CT-NA	1.453	337.0
NA-NA	1.392	400.0
CA-OS	1.316	320.0
OS-CT	1.416	320.0
CA-CC-L	131.3	rigid
CA-CC-CA	97.3	rigid
CA-NA-CT	120.9	70.0
CC-CA-NA	116.9	70.0
NA-NA-CA	104.1	70.0
NA-NA-CT	116.0	56.0
NA-CA-OS	114.0	80.0
CC-CA-OS	129.1	70.0
CA-OS-CT	116.7	60.0

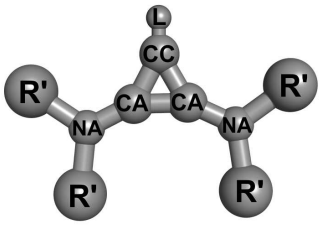

Figure 9: Structure of **9** with the names of the atoms.

Table 9: Bond stretching and angle bending parameters for **9**.

bond-/angletype	l_0 / θ_0 Å/ degree	k_l / k_θ kcal mol^{-1} Å^{-2} / kcal mol^{-1} rad^{-1}
CC-L	0.100	rigid
CC-CA	1.392	rigid
CA-CA	1.331	rigid
CA-NA	1.348	427.0
CT-NA	1.447	367.0
CA-CC-L	151.4	rigid
CA-CC-CA	57.1	rigid
CA-CA-CC	61.4	rigid
CC-CA-NA	145.1	70.0
CA-CA-NA	153.4	70.0
CA-NA-CT	118.5	50.0

2 CaFF Charges

Table 10: CaFF-charges for **1**.

Atom	Charge
L	−1.000
CC	0.000
NA	0.640
CW	−0.350
HA	0.210

Table 11: CaFF-charges for **2**.

Atom	Charge
L	−0.570
CC	−0.200
NA	0.780
S	0.160
CW1	−0.130
CW2	−0.380
HA1	0.160
HA2	0.180

CW1 next to S, HA1 next to CW1.

Table 12: CaFF-charges for **3**.

Atom	Charge
L	−0.620
CC	0.000
NA1	0.680
NA2	0.430
NA3	−0.620
CR	−0.050
HA	0.180

NA1 and NA2 next to CC, NA3 between NA2 and CR.

Table 13: CaFF-charges for **4**.

Atom	Charge
L	−0.400
CC	−0.850
CW	0.300
NA1	0.730
NA2	0.000
CR	−0.070
HA1	0.090
HA2	0.200

NA1 between CC and CR, HA1 next to CW, HA2 next to CR.

Table 14: CaFF-charges for **5**.

Atom	Charge
L	−0.480
CC	−0.400
NA	0.400
CT	−0.020
H1	0.030

Table 15: CaFF-charges for **6**.

Atom	Charge
L	−0.590
CC	−0.500
NA	0.940
CA1	−0.490
CA2	0.180
CA3	−0.370
CA4	0.460
HA1	0.190
HA2	0.060
HA3	0.160
HA4	−0.040

CAs are counted starting at the CA next to the NA, HAx next to CAx.

Table 16: CaFF-charges for **7**.

Atom	Charge
L	−1.040
CC	−0.100
NA	0.590
CT3	0.960
CT1	0.490
CT2	−0.400
CT4	−0.340
CT5	−0.320
HC1	0.050
HC2	0.060

CT1, CT2, CT3 are in the ring, counted from the NA.
HC1 are next to CT2.
HC2 are hydrogens on the methylgroups.
CT4 next to CT1, CT5 next to CT3.

Table 17: CaFF-charges for **8**.

Atom	Charge
L	0.200
CC	−1.700
CA	1.030
NA	−0.280
OS	−0.400
CT	0.110
H1	0.030

Table 18: CaFF-charges for **9**.

Atom	Charge
L	−0.200
CC	−0.800
CA	0.600
NA	−0.500

3 Non-Bonding Parameters Obtained by Fitting with Different Water Models

Table 19: Non-Bonding Parameters obtained by fitting with different three-site water models.

Water model	SPC/E	SPC	TIPS	TIP3P
Charge L	−1.00	−1.00	−0.50	−0.50
Charge CC	0.00	0.00	−0.50	−0.50
Charge NA	0.64	0.59	0.59	0.64
Charge CW	−0.35	−0.30	−0.30	−0.35
Charge HA	0.06	0.06	0.06	0.06
σ / Å	3.55	3.55	3.45	3.55
ϵ / kcal mol^{-1}	0.38	0.37	0.47	0.33

4 Geometrical Data Obtained using Different Methods

Table 20: Distances in the structure of **1** (R = Me) after optimization with different methods. Differences bigger than 0.02 Å compared to the HF/6-31G(d) level are highlighted.

atoms		HF	B3LYP-D3	BLYP-D3	PBE0-D3	PBE-D3	TPSS-D3	TPSSh-D3
CC	NA	1.35	1.36	**1.38**	1.36	1.37	**1.37**	1.37
CC	NA	1.35	1.36	**1.38**	1.36	1.37	**1.37**	1.37
NA	CW	1.38	1.39	1.40	1.38	1.39	1.39	1.39
NA	CT	1.44	1.45	1.46	1.44	1.45	1.46	1.45
CW	CW	1.33	1.35	**1.36**	1.35	**1.36**	**1.36**	**1.35**
CW	HA	1.07	1.08	1.08	1.08	1.08	1.08	1.08
CW	NA	1.38	1.39	1.40	1.38	1.39	1.39	1.39
CW	HA	1.07	1.08	1.08	1.08	1.09	1.08	1.08
NA	CT	1.44	1.45	1.46	1.44	1.45	1.46	1.45
CT	HC	1.08	1.09	1.09	1.09	1.09	1.09	1.09
CT	HC	1.08	1.09	1.10	1.09	1.10	1.10	1.09
CT	HC	1.08	1.09	1.10	1.09	1.10	1.10	1.09
CT	HC	1.08	1.09	1.09	1.09	1.09	1.09	1.09
CT	HC	1.08	1.09	1.10	1.09	1.10	1.10	1.09
CT	HC	1.08	1.09	1.10	1.09	1.10	1.10	1.09

atoms		B3LYP	BLYP	M06	MP2	PBE	PBE0	SCS-MP2	TPSS	TPSSh
CC	NA	**1.37**	**1.38**	1.36	1.37	1.37	1.36	1.37	**1.37**	1.37
CC	NA	**1.37**	**1.38**	1.36	1.37	1.37	1.36	1.37	**1.37**	1.37
NA	CW	1.39	1.40	1.38	1.38	1.39	1.38	1.38	1.39	1.39
NA	CT	1.45	1.46	1.44	1.45	1.45	1.44	1.45	1.46	1.45
CW	CW	**1.36**	**1.36**	1.35	**1.36**	**1.36**	1.35	**1.36**	**1.36**	**1.35**
CW	HA	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08
CW	NA	1.39	1.40	1.38	1.38	1.39	1.38	1.38	1.39	1.39
CW	HA	1.08	1.08	1.08	1.08	1.09	1.08	1.08	1.08	1.08
NA	CT	1.45	1.46	1.44	1.45	1.45	1.44	1.45	1.46	1.45
CT	HC	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09
CT	HC	1.10	1.10	1.09	1.09	1.10	1.09	1.09	1.10	1.09
CT	HC	1.10	1.10	1.09	1.09	1.10	1.09	1.09	1.10	1.09
CT	HC	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09
CT	HC	1.10	1.10	1.09	1.09	1.10	1.09	1.09	1.10	1.09
CT	HC	1.10	1.10	1.09	1.09	1.10	1.09	1.09	1.10	1.09

Table 21: Angles in the structure of **1** (R = Me) after optimization with different methods.

atoms			HF	B3LYP-D3	BLYP-D3	PBE0-D3	PBE-D3	TPSS-D3	TPSSh-D3
NA	CC	NA	102.5	102.15	101.82	102.05	101.71	101.44	101.62
NA	CC	NA	102.5	102.15	101.82	102.05	101.71	101.44	101.62
CW	NA	CC	112.5	112.83	113.02	112.96	113.17	113.24	113.14
CW	NA	CT	124.3	124.12	124.09	124.19	124.19	124.20	124.21
CT	NA	CC	123.3	123.05	122.90	122.85	122.64	122.55	122.64
CT	NA	CW	124.3	124.12	124.09	124.19	124.19	124.20	124.21
CW	CW	NA	106.3	106.09	106.06	106.01	105.97	106.03	106.04
CW	CW	HA	130.8	130.63	130.56	130.61	130.54	130.69	130.69
HA	CW	NA	123.0	123.29	123.38	123.39	123.49	123.28	123.27
HA	CW	CW	130.8	130.63	130.56	130.61	130.54	130.69	130.69
NA	CW	CW	106.3	106.09	106.07	106.01	105.98	106.03	106.04
NA	CW	HA	123.0	123.27	123.36	123.37	123.48	123.29	123.28
HA	CW	CW	130.8	130.64	130.57	130.62	130.55	130.67	130.67
HA	CW	NA	123.0	123.27	123.36	123.37	123.48	123.29	123.28
CT	NA	CC	123.3	123.05	122.89	122.84	122.62	122.54	122.63
CT	NA	CW	124.3	124.12	124.09	124.19	124.20	124.21	124.22
HC	CT	NA	107.8	107.61	107.48	107.48	107.33	107.16	107.24
HC	CT	HC	109.2	109.38	109.51	109.32	109.42	109.75	109.67
HC	CT	HC	109.2	109.38	109.51	109.32	109.42	109.75	109.67
HC	CT	NA	111.0	110.78	110.70	110.91	110.88	110.53	110.59
HC	CT	HC	109.2	109.38	109.51	109.32	109.42	109.75	109.67
HC	CT	HC	108.7	108.88	108.93	108.88	108.89	109.10	109.07
HC	CT	NA	111.0	110.78	110.70	110.91	110.88	110.53	110.59
HC	CT	HC	109.2	109.38	109.51	109.32	109.42	109.75	109.67
HC	CT	HC	108.7	108.88	108.93	108.88	108.89	109.10	109.07
HC	CT	NA	107.8	107.62	107.50	107.49	107.35	107.16	107.24
HC	CT	HC	109.2	109.35	109.46	109.29	109.38	109.73	109.66
HC	CT	HC	109.2	109.35	109.46	109.29	109.38	109.73	109.66
HC	CT	NA	111.0	110.79	110.70	110.91	110.88	110.53	110.59
HC	CT	HC	109.2	109.35	109.46	109.29	109.38	109.73	109.66
HC	CT	HC	108.7	108.92	108.99	108.91	108.94	109.13	109.09
HC	CT	NA	111.0	110.79	110.70	110.91	110.88	110.53	110.59
HC	CT	HC	109.2	109.35	109.46	109.29	109.38	109.73	109.66
HC	CT	HC	108.7	108.92	108.99	108.91	108.94	109.13	109.09

Table 22: Angles in the structure of **1** (R = Me) after optimization with different methods.

atoms			B3LYP	BLYP	M06	MP2	PBE	PBE0	SCS-MP2	TPSS	TPSSh
NA	CC	NA	101.45	101.93	102.10	101.42	101.75	102.08	101.69	101.49	101.68
NA	CC	NA	101.45	101.93	102.10	101.42	101.75	102.08	101.69	101.49	101.68
CW	NA	CC	113.24	112.92	112.92	113.47	113.13	112.92	113.24	113.19	113.09
CW	NA	CT	124.27	124.22	124.28	124.02	124.22	124.26	124.02	124.24	124.27
CT	NA	CC	122.49	122.86	122.80	122.51	122.65	122.81	122.74	122.57	122.64
CT	NA	CW	124.27	124.22	124.28	124.02	124.22	124.26	124.02	124.24	124.27
CW	CW	NA	106.03	106.11	106.00	105.82	105.98	106.03	105.91	106.05	106.07
CW	CW	HA	130.74	130.46	131.14	130.82	130.53	130.56	130.88	130.67	130.66
HA	CW	NA	123.22	123.43	122.86	123.36	123.49	123.41	123.21	123.28	123.28
HA	CW	CW	130.74	130.46	131.14	130.82	130.53	130.56	130.88	130.67	130.66
NA	CW	CW	106.03	106.12	106.11	105.82	105.99	106.03	105.91	106.06	106.07
NA	CW	HA	123.22	123.41	122.73	123.36	123.47	123.40	123.21	123.29	123.29
HA	CW	CW	130.75	130.47	131.16	130.82	130.54	130.57	130.88	130.65	130.64
HA	CW	NA	123.22	123.41	122.73	123.36	123.47	123.40	123.21	123.29	123.29
CT	NA	CC	122.46	122.85	123.55	122.51	122.63	122.80	122.74	122.55	122.63
CT	NA	CW	124.29	124.22	123.59	124.02	124.22	124.27	124.02	124.24	124.28
HC	CT	NA	107.30	107.52	107.88	107.29	107.36	107.46	107.41	107.20	107.25
HC	CT	HC	109.35	109.42	109.12	109.64	109.38	109.32	109.59	109.70	109.65
HC	CT	HC	109.35	109.42	109.12	109.63	109.38	109.32	109.60	109.70	109.65
HC	CT	NA	111.05	110.79	111.08	110.49	110.92	110.92	110.50	110.57	110.61
HC	CT	HC	109.35	109.42	109.12	109.64	109.38	109.32	109.59	109.70	109.65
HC	CT	HC	108.71	108.88	108.52	109.28	108.86	108.87	109.21	109.07	109.05
HC	CT	NA	111.05	110.79	111.08	110.48	110.92	110.92	110.49	110.57	110.61
HC	CT	HC	109.35	109.42	109.12	109.63	109.38	109.32	109.60	109.70	109.65
HC	CT	HC	108.71	108.88	108.52	109.28	108.86	108.87	109.21	109.07	109.05
HC	CT	NA	107.29	107.54	107.74	107.29	107.38	107.48	107.41	107.20	107.25
HC	CT	HC	109.33	109.37	108.84	109.64	109.34	109.29	109.59	109.69	109.63
HC	CT	HC	109.33	109.37	108.84	109.63	109.34	109.29	109.60	109.69	109.63
HC	CT	NA	111.06	110.80	111.16	110.49	110.92	110.92	110.50	110.57	110.61
HC	CT	HC	109.33	109.37	108.84	109.64	109.34	109.29	109.59	109.69	109.63
HC	CT	HC	108.74	108.94	109.06	109.28	108.91	108.91	109.21	109.10	109.07
HC	CT	NA	111.06	110.80	111.16	110.48	110.92	110.92	110.49	110.57	110.61
HC	CT	HC	109.33	109.37	108.84	109.63	109.34	109.29	109.60	109.69	109.63
HC	CT	HC	108.74	108.94	109.06	109.28	108.91	108.91	109.21	109.10	109.07

Table 23: Dihedrals in the structure of **1** (R = Me) after optimization with different methods.

atoms				HF	B3LYP-D3	BLYP-D3	PBE0-D3	PBE-D3	TPSS-D3	TPSSh-D3
HA	CW	NA	CC	180.0	180.00	180.00	180.00	180.00	180.00	180.00
HA	CW	NA	CT	0.0	0.00	0.00	0.00	0.00	0.00	0.00
HA	CW	CW	NA	180.0	180.00	180.00	180.00	180.00	180.00	180.00
HA	CW	CW	HA	0.0	0.00	0.00	0.00	0.00	0.00	0.00
HA	CW	CW	NA	180.0	180.00	180.00	180.00	180.00	180.00	180.00
HA	CW	CW	HA	0.0	0.00	0.00	0.00	0.00	0.00	0.00
HA	CW	NA	CC	180.0	180.00	180.00	180.00	180.00	180.00	180.00
HA	CW	NA	CT	0.0	0.00	0.00	0.00	0.00	0.00	0.00
HC	CT	NA	CC	0.0	0.00	0.00	0.00	0.00	0.00	0.00
HC	CT	NA	CW	180.0	180.00	180.00	180.00	180.00	180.00	180.00
HC	CT	NA	CC	119.5	119.53	119.55	119.45	119.46	119.56	119.54
HC	CT	NA	CW	60.5	60.47	60.45	60.55	60.54	60.44	60.46
HC	CT	NA	CC	119.5	119.53	119.55	119.45	119.46	119.56	119.54
HC	CT	NA	CW	60.5	60.47	60.45	60.55	60.54	60.44	60.46
HC	CT	NA	CC	0.0	0.00	0.00	0.00	0.00	0.00	0.00
HC	CT	NA	CW	180.0	180.00	180.00	180.00	180.00	180.00	180.00
HC	CT	NA	CC	119.5	119.50	119.51	119.42	119.42	119.54	119.52
HC	CT	NA	CW	60.5	60.50	60.49	60.58	60.58	60.46	60.48
HC	CT	NA	CC	119.5	119.50	119.51	119.42	119.42	119.54	119.52
HC	CT	NA	CW	60.5	60.50	60.49	60.58	60.58	60.46	60.48

Table 24: Dihedrals in the structure of **1** (R = Me) after optimization with different methods.

atoms				B3LYP	BLYP	M06	MP2	PBE	PBE0	SCS-MP2	TPSS	TPSSh
HA	CW	NA	CC	180.00	180.00	180.00	179.93	180.00	180.00	179.89	180.00	180.00
HA	CW	NA	CT	0.00	0.00	0.00	0.06	0.00	0.00	0.09	0.00	0.00
HA	CW	CW	NA	180.00	180.00	180.00	179.93	180.00	180.00	179.88	180.00	180.00
HA	CW	CW	HA	0.00	0.00	0.00	0.17	0.00	0.00	0.27	0.00	0.00
HA	CW	CW	NA	180.00	180.00	180.00	179.93	180.00	180.00	179.88	180.00	180.00
HA	CW	CW	HA	0.00	0.00	0.00	0.17	0.00	0.00	0.27	0.00	0.00
HA	CW	NA	CC	180.00	180.00	180.00	179.93	180.00	180.00	179.89	180.00	180.00
HA	CW	NA	CT	0.00	0.00	0.00	0.06	0.00	0.00	0.09	0.00	0.00
HC	CT	NA	CC	0.00	0.00	0.00	0.03	0.00	0.00	0.02	0.00	0.00
HC	CT	NA	CW	180.00	180.00	180.00	179.97	180.00	180.00	180.00	180.00	180.00
HC	CT	NA	CC	119.46	119.52	119.56	119.44	119.45	119.44	119.49	119.55	119.53
HC	CT	NA	CW	60.54	60.48	60.45	60.55	60.55	60.56	60.49	60.45	60.47
HC	CT	NA	CC	119.46	119.52	119.55	119.50	119.45	119.44	119.53	119.55	119.53
HC	CT	NA	CW	60.54	60.48	60.44	60.50	60.55	60.56	60.49	60.45	60.47
HC	CT	NA	CC	0.00	0.00	0.00	0.03	0.00	0.00	0.02	0.00	0.00
HC	CT	NA	CW	180.00	180.00	180.00	179.97	180.00	180.00	180.00	180.00	180.00
HC	CT	NA	CC	119.43	119.48	119.16	119.44	119.41	119.41	119.49	119.53	119.52
HC	CT	NA	CW	60.57	60.52	60.84	60.55	60.59	60.59	60.49	60.47	60.48
HC	CT	NA	CC	119.43	119.48	119.16	119.50	119.41	119.41	119.53	119.53	119.52
HC	CT	NA	CW	60.57	60.52	60.84	60.50	60.59	60.59	60.49	60.47	60.48

Table 25: Distances in the structure of **2** (R = Me) after optimization with different methods. Differences bigger than 0.02 Å compared to the HF/6-31G(d) level are highlighted.

atoms		HF	B3LYP-D3	BLYP-D3	PBE0-D3	PBE-D3	TPSS-D3	TPSSh-D3
NA	CC	1.33	**1.35**	**1.36**	1.34	**1.36**	**1.36**	**1.35**
NA	CW	1.40	1.40	1.41	1.39	1.40	1.40	1.39
NA	CT	1.46	1.47	1.47	1.45	1.46	1.47	1.46
CC	S	1.72	1.74	1.73	**1.70**	1.72	1.72	1.72
S	CW	1.74	1.75	1.76	1.73	1.74	1.74	1.73
CW	CW	1.33	**1.35**	**1.36**	1.34	**1.36**	**1.35**	**1.35**
CW	HA	1.07	1.08	1.08	1.08	1.09	1.08	1.08
CW	HA	1.07	1.08	1.09	1.08	1.09	1.08	1.08
CT	HC	1.08	1.09	1.09	1.09	1.09	1.09	1.09
CT	HC	1.08	1.10	1.10	1.09	1.10	1.09	1.09
CT	HC	1.08	1.10	1.10	1.09	1.10	1.09	1.09

atoms		B3LYP	BLYP	M06	MP2	PBE	PBE0	SCS-MP2	TPSS	TPSSh
NA	CC	**1.35**	**1.36**	1.34	**1.35**	**1.36**	1.34	1.35	**1.36**	**1.35**
NA	CW	1.40	1.41	1.38	1.38	1.40	1.39	1.39	1.40	1.39
NA	CT	1.47	**1.48**	1.44	1.46	1.46	1.45	1.46	1.47	1.47
CC	S	1.74	1.73	**1.69**	1.71	1.72	**1.70**	1.71	1.72	1.72
S	CW	1.75	1.76	**1.72**	**1.72**	1.74	1.73	1.73	1.74	1.73
CW	CW	**1.35**	**1.36**	1.34	**1.36**	**1.36**	1.34	**1.36**	**1.35**	**1.35**
CW	HA	1.08	1.08	1.08	1.08	1.09	1.08	1.08	1.08	1.08
CW	HA	1.08	1.09	1.08	1.08	1.09	1.08	1.08	1.08	1.08
CT	HC	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09
CT	HC	1.10	1.10	1.09	1.09	1.10	1.09	1.09	1.09	1.09
CT	HC	1.10	1.10	1.09	1.09	1.10	1.09	1.09	1.09	1.09

Table 26: Angles in the structure of **2** (R = Me) after optimization with different methods.

atoms			HF	B3LYP-D3	BLYP-D3	PBE0-D3	PBE-D3	TPSS-D3	TPSSh-D3
CC	NA	CW	118.5	119.37	118.92	118.65	118.90	119.11	118.97
CC	NA	CT	121.1	120.35	120.83	120.98	120.71	120.42	120.57
CW	NA	CC	118.5	119.37	118.92	118.65	118.90	119.11	118.97
CW	NA	CT	120.4	120.29	120.25	120.37	120.39	120.46	120.46
CT	NA	CC	121.1	120.35	120.83	120.98	120.71	120.42	120.57
CT	NA	CW	120.4	120.29	120.25	120.37	120.39	120.46	120.46
S	CC	NA	105.9	104.77	105.24	105.43	105.08	104.76	104.96
CW	S	CC	94.3	95.22	95.32	95.60	95.82	95.78	95.70
CW	CW	S	108.6	108.34	108.23	108.08	107.99	108.19	108.19
CW	CW	HA	127.4	127.33	127.23	127.25	127.25	127.22	127.21
HA	CW	S	123.9	124.33	124.54	124.67	124.76	124.59	124.60
HA	CW	CW	127.4	127.33	127.23	127.25	127.25	127.22	127.21
HA	CW	NA	119.5	119.73	119.93	119.98	120.07	119.88	119.87
HA	CW	CW	127.9	127.96	127.77	127.77	127.71	127.97	127.94
HC	CT	NA	107.9	107.31	107.49	107.53	107.37	107.07	107.17
HC	CT	HC	109.6	109.74	109.85	109.67	109.76	110.15	110.05
HC	CT	HC	109.6	109.74	109.85	109.67	109.76	110.15	110.05
HC	CT	NA	110.4	110.44	110.16	110.39	110.35	109.98	110.05
HC	CT	HC	109.6	109.74	109.85	109.67	109.76	110.15	110.05
HC	CT	HC	109.1	109.16	109.31	109.18	109.23	109.50	109.43
HC	CT	NA	110.4	110.44	110.16	110.39	110.35	109.98	110.05
HC	CT	HC	109.6	109.74	109.85	109.67	109.76	110.15	110.05
HC	CT	HC	109.1	109.16	109.31	109.18	109.23	109.50	109.43

Table 27: Angles in the structure of **2** (R = Me) after optimization with different methods.

atoms			B3LYP	BLYP	M06	MP2	PBE	PBE0	SCS-MP2	TPSS	TPSSh
CC	NA	CW	119.37	118.77	118.51	119.15	118.83	118.59	118.98	119.04	118.87
CC	NA	CT	120.35	120.85	120.96	120.55	120.72	121.00	120.77	120.46	120.62
CW	NA	CC	119.37	118.77	118.51	119.15	118.83	118.59	118.98	119.04	118.87
CW	NA	CT	120.29	120.37	120.53	120.30	120.44	120.41	120.25	120.50	120.52
CT	NA	CC	120.35	120.85	120.96	120.55	120.72	121.00	120.77	120.46	120.62
CT	NA	CW	120.29	120.37	120.53	120.30	120.44	120.41	120.25	120.50	120.52
S	CC	NA	104.77	105.28	105.30	104.83	105.09	105.44	105.13	104.77	105.00
CW	S	CC	95.22	95.35	95.97	96.13	95.84	95.61	95.68	95.82	95.71
CW	CW	S	108.34	108.16	107.67	108.11	107.96	108.05	108.30	108.13	108.16
CW	CW	HA	127.33	127.27	128.25	127.06	127.30	127.27	127.10	127.30	127.24
HA	CW	S	124.33	124.57	124.08	124.83	124.75	124.68	124.60	124.57	124.60
HA	CW	CW	127.33	127.27	128.25	127.06	127.30	127.27	127.10	127.30	127.24
HA	CW	NA	119.73	119.92	119.70	120.17	120.04	119.99	119.93	119.84	119.87
HA	CW	CW	127.96	127.65	127.75	128.04	127.67	127.70	128.15	127.93	127.87
HC	CT	NA	107.31	107.52	107.71	107.29	107.40	107.55	107.45	107.10	107.21
HC	CT	HC	109.74	109.77	109.40	110.03	109.72	109.64	110.01	110.10	110.00
HC	CT	HC	109.74	109.77	109.40	110.05	109.72	109.64	110.00	110.10	110.00
HC	CT	NA	110.44	110.25	110.37	109.93	110.39	110.42	109.93	110.02	110.11
HC	CT	HC	109.74	109.77	109.40	110.03	109.72	109.64	110.01	110.10	110.00
HC	CT	HC	109.16	109.27	109.57	109.58	109.21	109.15	109.51	109.47	109.39
HC	CT	NA	110.44	110.25	110.37	109.93	110.39	110.42	109.92	110.02	110.11
HC	CT	HC	109.74	109.77	109.40	110.05	109.72	109.64	110.00	110.10	110.00
HC	CT	HC	109.16	109.27	109.57	109.58	109.21	109.15	109.51	109.47	109.39

Table 28: Dihedrals in the structure of **2** (R = Me) after optimization with different methods.

atoms				HF	B3LYP-D3	BLYP-D3	PBE0-D3	PBE-D3	TPSS-D3	TPSSh-D3
HA	CW	S	CC	180.0	180.00	180.00	179.98	180.00	179.98	180.00
HA	CW	CW	NA	180.0	180.00	180.00	179.99	180.00	179.99	180.00
HA	CW	CW	HA	0.0	0.00	0.00	0.00	0.00	0.00	0.00
HA	CW	NA	CC	180.0	180.00	180.00	179.99	180.00	179.99	180.00
HA	CW	NA	CT	0.0	0.00	0.00	0.00	0.00	0.00	0.00
HA	CW	CW	S	180.0	180.00	180.00	179.99	180.00	179.99	180.00
HA	CW	CW	HA	0.0	0.00	0.00	0.00	0.00	0.00	0.00
HC	CT	NA	CC	0.0	0.00	0.00	0.00	0.00	0.00	0.00
HC	CT	NA	CW	180.0	180.00	180.00	180.00	180.00	180.00	180.00
HC	CT	NA	CC	119.7	119.58	119.66	119.61	119.59	119.67	119.66
HC	CT	NA	CW	60.3	60.42	60.34	60.40	60.41	60.34	60.34
HC	CT	NA	CC	119.7	119.58	119.66	119.60	119.59	119.66	119.66
HC	CT	NA	CW	60.3	60.42	60.34	60.39	60.41	60.33	60.34

Table 29: Dihedrals in the structure of **2** (R = Me) after optimization with different methods.

atoms				B3LYP	BLYP	M06	MP2	PBE	PBE0	SCS-MP2	TPSS	TPSSh
HA	CW	S	CC	180.00	180.00	179.99	179.98	180.00	179.98	179.99	180.00	179.93
HA	CW	CW	NA	180.00	180.00	179.99	179.99	180.00	179.99	179.99	180.00	179.97
HA	CW	CW	HA	0.00	0.00	0.00	0.04	0.00	0.00	0.02	0.00	0.01
HA	CW	NA	CC	180.00	180.00	179.99	179.99	180.00	179.99	179.99	180.00	179.96
HA	CW	NA	CT	0.00	0.00	0.00	0.03	0.00	0.00	0.01	0.00	0.01
HA	CW	CW	S	180.00	180.00	179.99	179.97	180.00	179.99	179.99	180.00	179.95
HA	CW	CW	HA	0.00	0.00	0.00	0.04	0.00	0.00	0.02	0.00	0.01
HC	CT	NA	CC	0.00	0.00	0.00	0.02	0.00	0.00	0.02	0.00	0.02
HC	CT	NA	CW	180.00	180.00	180.00	179.96	180.00	180.00	180.00	180.00	179.98
HC	CT	NA	CC	119.58	119.64	119.37	119.66	119.58	119.59	119.68	119.65	119.64
HC	CT	NA	CW	60.42	60.36	60.63	60.32	60.42	60.40	60.30	60.35	60.33
HC	CT	NA	CC	119.58	119.64	119.37	119.63	119.58	119.60	119.70	119.65	119.67
HC	CT	NA	CW	60.42	60.36	60.63	60.39	60.42	60.41	60.31	60.35	60.36

Table 30: Distances in the structure of **3** (R = Me) after optimization with different methods. Differences bigger than 0.02 Å compared to the HF/6-31G(d) level are highlighted.

atoms		HF	B3LYP-D3	BLYP-D3	PBE0-D3	PBE-D3	TPSS-D3	TPSSh-D3
NA	CC	1.36	1.37	**1.38**	1.37	1.38	1.38	1.38
NA	CR	1.36	1.37	1.38	1.36	1.38	1.38	1.37
NA	CT	1.45	1.45	1.46	1.44	1.45	1.46	1.45
CC	NA	1.33	1.34	**1.36**	1.34	**1.35**	**1.35**	1.35
NA	NA	1.37	1.38	**1.40**	1.36	1.38	**1.39**	1.38
NA	CT	1.44	1.45	1.46	1.44	1.45	1.45	1.45
NA	CR	1.27	**1.30**	**1.31**	**1.29**	**1.31**	**1.31**	**1.30**
CR	HA	1.07	1.08	1.08	1.08	1.09	1.08	1.08
CT	HC	1.08	1.09	1.09	1.09	1.09	1.09	1.09
CT	HC	1.08	1.09	1.10	1.09	1.10	1.09	1.09
CT	HC	1.08	1.09	1.10	1.09	1.10	1.09	1.09
CT	HC	1.08	1.09	1.09	1.09	1.09	1.09	1.09
CT	HC	1.08	1.09	1.10	1.09	1.10	1.09	1.09
CT	HC	1.08	1.09	1.10	1.09	1.10	1.09	1.09

atoms		B3LYP	BLYP	M06	MP2	PBE	PBE0	SCS-MP2	TPSS	TPSSh
NA	CC	1.38	**1.39**	1.36	1.37	1.38	1.37	1.38	1.38	1.38
NA	CR	1.38	**1.38**	1.36	1.36	1.38	1.36	1.37	1.38	1.37
NA	CT	1.45	1.46	1.44	1.45	1.45	1.44	1.45	1.46	1.46
CC	NA	**1.35**	**1.36**	1.34	1.35	**1.35**	1.34	1.35	**1.35**	1.35
NA	NA	**1.39**	**1.40**	1.37	1.36	1.38	1.36	1.37	**1.39**	1.38
NA	CT	1.45	1.46	1.44	1.45	1.45	1.44	1.45	1.46	1.45
NA	CR	**1.30**	**1.31**	1.29	**1.31**	**1.31**	**1.29**	**1.31**	**1.31**	**1.30**
CR	HA	1.08	1.08	1.08	1.08	1.09	1.08	1.08	1.08	1.08
CT	HC	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09
CT	HC	1.09	1.10	1.09	1.09	1.10	1.09	1.09	1.09	1.09
CT	HC	1.09	1.10	1.09	1.09	1.10	1.09	1.09	1.09	1.09
CT	HC	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09
CT	HC	1.10	1.10	1.09	1.09	1.10	1.09	1.09	1.09	1.09
CT	HC	1.10	1.10	1.09	1.09	1.10	1.09	1.09	1.09	1.09

Table 31: Angles of the structure of **3** (R = Me) after optimization with different methods.

atoms			HF	B3LYP-D3	BLYP-D3	PBE0-D3	PBE-D3	TPSS-D3	TPSSh-D3
CC	NA	CR	109.5	110.11	110.33	110.13	110.39	110.43	110.31
CC	NA	CT	124.6	124.27	124.09	124.12	123.90	123.76	123.87
CR	NA	CC	109.5	110.11	110.33	110.13	110.39	110.43	110.31
CR	NA	CT	125.9	125.62	125.58	125.75	125.71	125.81	125.82
CT	NA	CC	124.6	124.27	124.09	124.12	123.90	123.76	123.87
CT	NA	CR	125.9	125.62	125.58	125.75	125.71	125.81	125.82
NA	CC	NA	100.7	100.61	100.46	100.38	100.17	99.99	100.10
NA	NA	CC	115.4	115.68	115.86	115.97	116.23	116.31	116.19
NA	NA	CT	118.4	118.34	118.09	118.46	118.24	118.04	118.15
CT	NA	CC	126.2	125.98	126.04	125.57	125.53	125.65	125.65
CT	NA	NA	118.4	118.34	118.09	118.46	118.24	118.04	118.15
CR	NA	NA	103.2	102.72	102.23	102.73	102.27	102.08	102.31
HA	CR	NA	124.2	124.62	124.62	124.76	124.81	124.60	124.62
HA	CR	NA	124.6	124.49	124.28	124.46	124.25	124.21	124.29
HC	CT	NA	107.8	107.61	107.51	107.54	107.44	107.19	107.26
HC	CT	HC	109.8	109.99	110.08	109.96	110.03	110.34	110.28
HC	CT	HC	109.8	109.99	110.08	109.96	110.03	110.34	110.28
HC	CT	NA	110.2	110.12	110.05	110.21	110.19	109.85	109.90
HC	CT	HC	109.8	109.99	110.08	109.96	110.03	110.34	110.28
HC	CT	HC	108.9	109.01	109.06	108.96	108.96	109.25	109.21
HC	CT	NA	110.2	110.12	110.05	110.21	110.19	109.85	109.90
HC	CT	HC	109.8	109.99	110.08	109.96	110.03	110.34	110.28
HC	CT	HC	108.9	109.01	109.06	108.96	108.96	109.25	109.21
HC	CT	NA	107.6	107.52	107.41	107.42	107.32	107.12	107.19
HC	CT	HC	109.2	109.34	109.47	109.27	109.38	109.70	109.62
HC	CT	HC	109.2	109.34	109.47	109.27	109.38	109.70	109.62
HC	CT	NA	110.9	110.75	110.65	110.87	110.81	110.48	110.55
HC	CT	HC	109.2	109.34	109.47	109.27	109.38	109.70	109.62
HC	CT	HC	109.0	109.12	109.16	109.10	109.10	109.33	109.29
HC	CT	NA	110.9	110.75	110.65	110.87	110.81	110.48	110.55
HC	CT	HC	109.2	109.34	109.47	109.27	109.38	109.70	109.62
HC	CT	HC	109.0	109.12	109.16	109.10	109.10	109.33	109.29

Table 32: Angles of the structure of **3** (R = Me) after optimization with different methods.

atoms			B3LYP	BLYP	M06	MP2	PBE	PBE0	SCS-MP2	TPSS	TPSSh
CC	NA	CR	110.37	110.20	109.98	110.67	110.32	110.07	110.39	110.36	110.22
CC	NA	CT	123.80	124.10	124.78	123.77	123.92	124.14	123.97	123.79	123.89
CR	NA	CC	110.37	110.20	109.98	110.67	110.32	110.07	110.39	110.36	110.22
CR	NA	CT	125.84	125.70	125.24	125.54	125.76	125.79	125.62	125.85	125.89
CT	NA	CC	123.80	124.10	124.78	123.77	123.92	124.14	123.97	123.79	123.89
CT	NA	CR	125.84	125.70	125.24	125.54	125.76	125.79	125.62	125.85	125.89
NA	CC	NA	99.90	100.56	100.45	99.79	100.22	100.42	100.05	100.04	100.16
NA	NA	CC	116.33	115.81	115.90	116.72	116.21	115.96	116.47	116.28	116.17
NA	NA	CT	118.09	118.16	118.47	118.01	118.26	118.48	118.00	118.07	118.16
CT	NA	CC	125.59	126.03	125.63	125.27	125.53	125.57	125.53	125.65	125.67
CT	NA	NA	118.09	118.16	118.47	118.01	118.26	118.48	118.00	118.07	118.16
CR	NA	NA	102.27	102.22	102.66	102.13	102.26	102.72	102.14	102.06	102.27
HA	CR	NA	124.50	124.63	124.17	124.98	124.79	124.77	124.75	124.56	124.61
HA	CR	NA	124.37	124.15	124.83	124.33	124.21	124.40	124.31	124.18	124.21
HC	CT	NA	107.42	107.56	107.76	107.31	107.47	107.57	107.40	107.22	107.29
HC	CT	HC	109.96	110.01	109.55	110.32	110.00	109.93	110.26	110.31	110.26
HC	CT	HC	109.96	110.01	109.55	110.37	110.00	109.93	110.31	110.31	110.26
HC	CT	NA	110.31	110.12	110.58	109.70	110.22	110.23	109.74	109.89	109.92
HC	CT	HC	109.96	110.01	109.55	110.32	110.00	109.93	110.26	110.31	110.26
HC	CT	HC	108.88	109.00	108.81	109.40	108.93	108.94	109.37	109.22	109.19
HC	CT	NA	110.31	110.12	110.58	109.71	110.22	110.23	109.73	109.89	109.92
HC	CT	HC	109.96	110.01	109.55	110.37	110.00	109.93	110.31	110.31	110.26
HC	CT	HC	108.88	109.00	108.81	109.40	108.93	108.94	109.37	109.22	109.19
HC	CT	NA	107.21	107.45	107.72	107.51	107.34	107.44	107.58	107.15	107.19
HC	CT	HC	109.34	109.40	109.12	109.73	109.35	109.24	109.66	109.66	109.60
HC	CT	HC	109.34	109.40	109.12	109.44	109.35	109.24	109.43	109.66	109.60
HC	CT	NA	110.97	110.73	111.01	110.09	110.85	110.90	110.09	110.52	110.57
HC	CT	HC	109.34	109.40	109.12	109.73	109.35	109.24	109.66	109.66	109.60
HC	CT	HC	108.98	109.11	108.82	109.45	109.07	109.07	109.39	109.30	109.28
HC	CT	NA	110.97	110.73	111.01	110.59	110.85	110.90	110.65	110.52	110.57
HC	CT	HC	109.34	109.40	109.12	109.44	109.35	109.24	109.43	109.66	109.60
HC	CT	HC	108.98	109.11	108.82	109.45	109.07	109.07	109.39	109.30	109.28

Table 33: Dihedrals of the structure of **3** (R = Me) after optimization with different methods.

atoms				HF	B3LYP-D3	BLYP-D3	PBE0-D3	PBE-D3	TPSS-D3	TPSSh-D3
HA	CR	NA	CC	180.0	180.00	180.00	180.00	180.00	180.00	180.00
HA	CR	NA	CT	0.0	0.00	0.00	0.00	0.00	0.00	0.00
HA	CR	NA	NA	180.0	180.00	180.00	180.00	180.00	180.00	180.00
HC	CT	NA	CC	0.0	0.00	0.00	0.00	0.00	0.00	0.00
HC	CT	NA	NA	180.0	180.00	180.00	180.00	180.00	180.00	180.00
HC	CT	NA	CC	119.8	119.88	119.89	119.85	119.87	119.90	119.90
HC	CT	NA	NA	60.2	60.12	60.11	60.15	60.13	60.10	60.10
HC	CT	NA	CC	119.8	119.88	119.89	119.85	119.87	119.90	119.90
HC	CT	NA	NA	60.2	60.12	60.11	60.15	60.13	60.10	60.10
HC	CT	NA	CC	0.0	0.00	0.00	0.00	0.00	0.00	0.00
HC	CT	NA	CR	180.0	180.00	180.00	180.00	180.00	180.00	180.00
HC	CT	NA	CC	119.4	119.40	119.44	119.33	119.37	119.45	119.43
HC	CT	NA	CR	60.6	60.60	60.56	60.67	60.63	60.55	60.58
HC	CT	NA	CC	119.4	119.40	119.44	119.33	119.37	119.45	119.42
HC	CT	NA	CR	60.6	60.60	60.56	60.67	60.63	60.55	60.57

Table 34: Dihedrals of the structure of **3** (R = Me) after optimization with different methods.

atoms				B3LYP	BLYP	M06	MP2	PBE	PBE0	SCS-MP2	TPSS	TPSSh
HA	CR	NA	CC	180.00	180.00	180.00	179.88	180.00	180.00	179.89	180.00	180.00
HA	CR	NA	CT	0.00	0.00	0.00	1.60	0.00	0.00	1.67	0.00	0.00
HA	CR	NA	NA	180.00	180.00	180.00	179.89	180.00	180.00	179.88	180.00	180.00
HC	CT	NA	CC	0.00	0.00	0.00	0.05	0.00	0.00	0.04	0.00	0.00
HC	CT	NA	NA	180.00	180.00	180.00	179.64	180.00	180.00	179.62	180.00	180.00
HC	CT	NA	CC	119.84	119.88	119.71	119.92	119.86	119.85	119.83	119.90	119.90
HC	CT	NA	NA	60.16	60.12	60.29	60.49	60.14	60.15	60.51	60.10	60.10
HC	CT	NA	CC	119.84	119.88	119.71	119.88	119.86	119.85	119.96	119.90	119.90
HC	CT	NA	NA	60.16	60.12	60.29	59.71	60.14	60.15	59.70	60.10	60.10
HC	CT	NA	CC	0.00	0.00	0.00	15.53	0.00	0.00	15.62	0.00	0.00
HC	CT	NA	CR	180.00	180.00	180.00	166.14	180.00	180.00	166.14	180.00	180.00
HC	CT	NA	CC	119.34	119.42	119.41	135.02	119.36	119.33	135.08	119.44	119.42
HC	CT	NA	CR	60.66	60.58	60.59	46.65	60.64	60.67	46.68	60.56	60.58
HC	CT	NA	CC	119.34	119.42	119.41	103.90	119.36	119.33	103.88	119.44	119.42
HC	CT	NA	CR	60.66	60.58	60.59	74.43	60.64	60.67	74.36	60.56	60.58

Table 35: Distances in the structure of **4** (R = Me) after optimization with different methods. Differences bigger than 0.02 Å compared to the HF/6-31G(d) level are highlighted.

atoms		HF	B3LYP-D3	BLYP-D3	PBE0-D3	PBE-D3	TPSS-D3	TPSSh-D3
NA	CR	1.32	**1.35**	**1.35**	1.33	**1.35**	**1.35**	**1.34**
NA	CC	1.42	1.42	1.42	1.40	1.41	1.42	1.41
NA	CT	1.45	1.46	1.46	1.44	1.45	1.46	1.46
CR	NA	1.31	**1.34**	**1.35**	1.33	**1.34**	**1.34**	**1.34**
CR	HA	1.07	1.08	1.08	1.08	1.09	1.08	1.08
NA	CW	1.40	1.40	1.41	1.39	1.40	1.40	1.40
NA	CT	1.45	1.46	1.46	1.44	1.45	1.46	1.46
CW	CC	1.37	1.39	**1.39**	1.38	**1.39**	1.39	1.38
CW	HA	1.07	1.08	1.08	1.08	1.09	1.08	1.08
CT	HC	1.08	1.09	1.09	1.09	1.10	1.09	1.09
CT	HC	1.08	1.09	1.10	1.09	1.10	1.09	1.09
CT	HC	1.08	1.09	1.10	1.09	1.10	1.09	1.09
CT	HC	1.08	1.09	1.10	1.09	1.10	1.09	1.09
CT	HC	1.08	1.09	1.10	1.09	1.10	1.09	1.09
CT	HC	1.08	1.09	1.10	1.09	1.10	1.09	1.09

atoms		B3LYP	BLYP	M06	MP2	PBE	PBE0	SCS-MP2	TPSS	TPSSh
NA	CR	**1.34**	**1.35**	1.33	**1.35**	**1.35**	1.33	**1.34**	**1.35**	**1.34**
NA	CC	1.41	1.42	**1.39**	1.40	1.41	1.40	1.41	1.42	1.41
NA	CT	1.45	1.47	1.44	1.45	1.46	1.44	1.46	1.46	1.46
CR	NA	**1.33**	**1.35**	1.33	**1.34**	**1.34**	1.33	**1.34**	**1.34**	**1.33**
CR	HA	1.08	1.08	1.08	1.08	1.09	1.08	1.08	1.08	1.08
NA	CW	1.40	1.41	1.39	1.38	1.40	1.39	1.39	1.40	1.40
NA	CT	1.45	**1.47**	1.43	1.45	1.45	1.44	1.45	1.46	1.46
CW	CC	1.38	**1.39**	1.37	**1.39**	**1.39**	1.38	**1.39**	1.39	1.38
CW	HA	1.08	1.08	1.08	1.08	1.09	1.08	1.08	1.08	1.08
CT	HC	1.09	1.09	1.09	1.09	1.10	1.09	1.09	1.09	1.09
CT	HC	1.09	1.10	1.09	1.09	1.10	1.09	1.09	1.09	1.09
CT	HC	1.09	1.10	1.09	1.09	1.10	1.09	1.09	1.09	1.09
CT	HC	1.09	1.10	1.09	1.09	1.10	1.09	1.09	1.09	1.09
CT	HC	1.09	1.10	1.09	1.09	1.10	1.09	1.09	1.09	1.09
CT	HC	1.09	1.10	1.09	1.09	1.10	1.09	1.09	1.09	1.09

Table 36: Angles in the structure of **4** (R = Me) after optimization with different methods.

atoms			HF	B3LYP-D3	BLYP-D3	PBE0-D3	PBE-D3	TPSS-D3	TPSSh-D3
CR	NA	CC	112.9	113.81	113.42	113.41	113.58	113.61	113.53
CR	NA	CT	124.6	123.90	123.76	123.76	123.52	123.53	123.60
CC	NA	CR	112.9	113.81	113.42	113.41	113.58	113.61	113.53
CC	NA	CT	122.5	122.29	122.83	122.82	122.88	122.85	122.86
CT	NA	CR	124.6	123.90	123.76	123.76	123.52	123.53	123.60
CT	NA	CC	122.5	122.29	122.83	122.82	122.88	122.85	122.86
NA	CR	NA	108.5	107.10	106.97	107.22	106.88	107.10	107.22
NA	CR	HA	125.0	125.14	125.08	125.12	125.01	125.02	125.08
HA	CR	NA	126.5	127.76	127.95	127.66	128.11	127.87	127.70
HA	CR	NA	125.0	125.14	125.08	125.12	125.01	125.02	125.08
CW	NA	CR	106.9	107.09	107.36	107.36	107.38	107.20	107.21
CW	NA	CT	126.6	127.12	126.93	126.87	127.05	127.43	127.32
CT	NA	CR	126.5	125.80	125.70	125.77	125.57	125.36	125.46
CT	NA	CW	126.6	127.12	126.93	126.87	127.05	127.43	127.32
CC	CW	NA	111.4	111.94	111.38	111.28	111.43	111.68	111.59
CC	CW	HA	129.9	129.82	129.91	129.75	129.78	129.84	129.83
HA	CW	NA	118.6	118.24	118.71	118.97	118.79	118.47	118.57
HA	CW	CC	129.9	129.82	129.91	129.75	129.78	129.84	129.83
HC	CT	NA	109.8	109.95	109.83	109.85	109.90	109.45	109.48
HC	CT	HC	109.0	108.88	108.99	108.86	109.00	109.21	109.15
HC	CT	HC	109.0	108.88	109.17	108.94	108.91	109.28	109.22
HC	CT	NA	110.0	110.13	109.60	110.02	110.20	109.63	109.74
HC	CT	HC	109.0	108.88	108.99	108.86	109.00	109.21	109.15
HC	CT	HC	109.1	108.83	108.98	108.89	108.87	109.25	109.21
HC	CT	NA	110.0	110.13	110.25	110.26	109.92	110.00	110.03
HC	CT	HC	109.0	108.88	109.17	108.94	108.91	109.28	109.22
HC	CT	HC	109.1	108.83	108.98	108.89	108.87	109.25	109.21
HC	CT	NA	110.3	110.47	110.12	110.31	110.36	109.87	109.91
HC	CT	HC	109.3	109.54	109.78	109.65	110.00	110.06	109.92
HC	CT	HC	109.3	109.54	109.76	109.58	109.47	109.78	109.77
HC	CT	NA	109.5	109.44	109.26	109.25	108.35	108.69	108.94
HC	CT	HC	109.3	109.54	109.78	109.65	110.00	110.06	109.92
HC	CT	HC	108.7	108.39	108.56	108.45	108.50	108.88	108.83
HC	CT	NA	109.5	109.44	109.34	109.58	110.13	109.53	109.44
HC	CT	HC	109.3	109.54	109.76	109.58	109.47	109.78	109.77
HC	CT	HC	108.7	108.39	108.56	108.45	108.50	108.88	108.83

Table 37: Angles in the structure of **4** (R = Me) after optimization with different methods.

atoms			B3LYP	BLYP	M06	MP2	PBE	PBE0	SCS-MP2	TPSS	TPSSh
CR	NA	CC	113.16	113.31	113.36	114.14	113.53	113.38	113.85	113.53	113.46
CR	NA	CT	123.94	123.80	124.87	123.09	123.54	123.77	123.45	123.54	123.59
CC	NA	CR	113.16	113.31	113.36	114.14	113.53	113.38	113.85	113.53	113.46
CC	NA	CT	122.90	122.89	121.77	122.72	122.91	122.85	122.70	122.91	122.93
CT	NA	CR	123.94	123.80	124.87	123.09	123.54	123.77	123.45	123.54	123.59
CT	NA	CC	122.90	122.89	121.77	122.72	122.91	122.85	122.70	122.91	122.93
NA	CR	NA	107.41	107.15	107.16	106.36	106.98	107.29	106.83	107.22	107.33
NA	CR	HA	125.10	125.00	125.29	125.57	124.97	125.15	125.44	124.95	124.99
HA	CR	NA	127.49	127.85	127.55	128.07	128.06	127.55	127.73	127.84	127.68
HA	CR	NA	125.10	125.00	125.29	125.57	124.97	125.15	125.44	124.95	124.99
CW	NA	CR	107.18	107.15	107.36	107.57	107.27	107.26	107.38	107.09	107.11
CW	NA	CT	126.90	127.10	125.80	126.90	127.13	126.91	126.95	127.52	127.42
CT	NA	CR	125.91	125.73	126.83	125.41	125.61	125.83	125.66	125.38	125.47
CT	NA	CW	126.90	127.10	125.80	126.90	127.13	126.91	126.95	127.52	127.42
CC	CW	NA	111.35	111.52	111.28	111.75	111.51	111.37	111.73	111.75	111.67
CC	CW	HA	129.71	129.68	130.14	129.44	129.67	129.67	129.45	129.71	129.73
HA	CW	NA	118.94	118.80	118.57	118.81	118.82	118.96	118.82	118.54	118.60
HA	CW	CC	129.71	129.68	130.14	129.44	129.67	129.67	129.45	129.71	129.73
HC	CT	NA	109.84	109.89	110.33	109.58	109.96	109.88	109.39	109.48	109.48
HC	CT	HC	108.92	108.89	108.87	108.97	108.95	108.89	109.16	109.20	109.16
HC	CT	HC	108.92	109.08	108.87	109.42	108.87	108.86	109.21	109.21	109.17
HC	CT	NA	110.11	109.67	110.00	109.11	110.25	110.18	109.77	109.85	109.88
HC	CT	HC	108.92	108.89	108.87	108.97	108.95	108.89	109.16	109.20	109.16
HC	CT	HC	108.90	108.92	108.75	109.31	108.84	108.87	109.36	109.21	109.19
HC	CT	NA	110.11	110.35	110.00	110.43	109.95	110.13	109.94	109.88	109.94
HC	CT	HC	108.92	109.08	108.87	109.42	108.87	108.86	109.21	109.21	109.17
HC	CT	HC	108.90	108.92	108.75	109.31	108.84	108.87	109.36	109.21	109.19
HC	CT	NA	110.25	110.24	110.87	110.04	110.43	110.34	109.86	109.98	110.01
HC	CT	HC	109.59	109.69	109.62	110.14	109.97	109.58	109.86	110.13	110.07
HC	CT	HC	109.59	109.68	109.62	109.73	109.44	109.59	109.88	109.64	109.60
HC	CT	NA	109.45	109.31	109.24	108.10	108.35	109.48	109.17	108.34	108.39
HC	CT	HC	109.59	109.69	109.62	110.14	109.97	109.58	109.86	110.13	110.07
HC	CT	HC	108.48	108.49	108.20	108.97	108.45	108.41	108.93	108.91	108.87
HC	CT	NA	109.45	109.41	109.24	109.84	110.17	109.41	109.11	109.83	109.88
HC	CT	HC	109.59	109.68	109.62	109.73	109.44	109.59	109.88	109.64	109.60
HC	CT	HC	108.48	108.49	108.20	108.97	108.45	108.41	108.93	108.91	108.87

Table 38: Dihedrals in the structure of **4** (R = Me) after optimization with different methods.

atoms				HF	B3LYP-D3	BLYP-D3	PBE0-D3	PBE-D3	TPSS-D3	TPSSh-D3
HA	CR	NA	CC	180.0	180.00	179.94	179.96	179.92	179.99	179.99
HA	CR	NA	CT	0.0	0.00	0.42	0.36	1.67	1.02	0.63
HA	CR	NA	CW	180.0	180.00	179.87	179.99	179.94	179.95	179.96
HA	CR	NA	CT	0.0	0.00	1.22	0.65	0.03	0.99	0.76
HA	CW	NA	CR	180.0	180.00	179.87	179.93	179.65	179.87	179.93
HA	CW	NA	CT	0.0	0.00	1.51	0.59	0.32	0.95	0.75
HA	CW	CC	NA	180.0	180.00	179.81	179.93	179.51	179.84	179.92
HC	CT	NA	CR	0.0	0.00	8.67	3.37	3.64	5.09	4.23
HC	CT	NA	CW	180.0	180.00	172.95	177.40	176.33	176.17	176.73
HC	CT	NA	CR	119.9	119.99	128.37	123.19	116.51	124.85	124.00
HC	CT	NA	CW	60.1	60.01	53.25	57.58	63.52	56.40	56.96
HC	CT	NA	CR	119.9	119.99	111.67	116.70	123.49	115.00	115.81
HC	CT	NA	CW	60.1	60.01	66.72	62.53	56.48	63.75	63.23
HC	CT	NA	CR	0.0	0.00	0.84	3.16	17.45	8.52	5.04
HC	CT	NA	CC	180.0	180.00	179.56	177.27	164.28	172.59	175.65
HC	CT	NA	CR	120.4	120.68	121.48	123.76	137.95	129.01	125.54
HC	CT	NA	CC	59.6	59.32	58.91	56.67	43.78	52.11	55.15
HC	CT	NA	CR	120.4	120.68	119.84	117.55	103.53	112.14	115.58
HC	CT	NA	CC	59.6	59.32	59.77	62.01	74.74	66.74	63.73

Table 39: Dihedrals in the structure of **4** (R = Me) after optimization with different methods.

atoms				B3LYP	BLYP	M06	MP2	PBE	PBE0	SCS-MP2	TPSS	TPSSh
HA	CR	NA	CC	180.00	180.00	180.00	180.00	179.88	180.00	179.79	179.87	179.89
HA	CR	NA	CT	0.00	0.35	0.00	2.51	1.68	0.12	0.31	1.60	1.59
HA	CR	NA	CW	180.00	179.92	180.00	179.79	179.90	179.99	179.81	179.85	179.86
HA	CR	NA	CT	0.00	1.26	0.00	3.50	0.03	0.11	0.50	0.47	0.48
HA	CW	NA	CR	180.00	179.88	180.00	179.82	179.67	179.98	179.97	179.76	179.76
HA	CW	NA	CT	0.00	1.49	0.00	3.60	0.26	0.15	0.29	0.40	0.40
HA	CW	CC	NA	180.00	179.82	180.00	179.83	179.53	179.98	179.99	179.66	179.66
HC	CT	NA	CR	0.00	8.95	0.00	20.72	3.83	0.80	2.24	0.78	0.90
HC	CT	NA	CW	180.00	172.66	180.00	163.70	176.09	179.35	178.13	179.97	179.84
HC	CT	NA	CR	119.95	128.62	120.12	139.95	116.32	119.17	121.99	120.68	120.78
HC	CT	NA	CW	60.05	52.99	59.88	44.47	63.76	60.67	58.38	60.06	59.97
HC	CT	NA	CR	119.95	111.38	120.12	99.88	123.68	120.71	117.68	119.16	119.02
HC	CT	NA	CW	60.05	67.01	59.88	75.70	56.24	59.44	61.95	60.10	60.23
HC	CT	NA	CR	0.00	0.94	0.00	19.27	17.72	0.75	0.83	15.43	15.11
HC	CT	NA	CC	180.00	179.44	180.00	163.45	163.98	179.38	179.28	166.18	166.51
HC	CT	NA	CR	120.61	121.59	120.91	139.58	138.22	119.93	119.71	135.84	135.50
HC	CT	NA	CC	59.39	58.79	59.09	43.13	43.49	59.94	60.18	45.77	46.12
HC	CT	NA	CR	120.61	119.75	120.91	101.64	103.29	121.40	121.35	105.31	105.64
HC	CT	NA	CC	59.39	59.87	59.09	75.64	75.01	58.73	58.76	73.08	72.74

5 Overview of Partial Atomic Charges with Different R

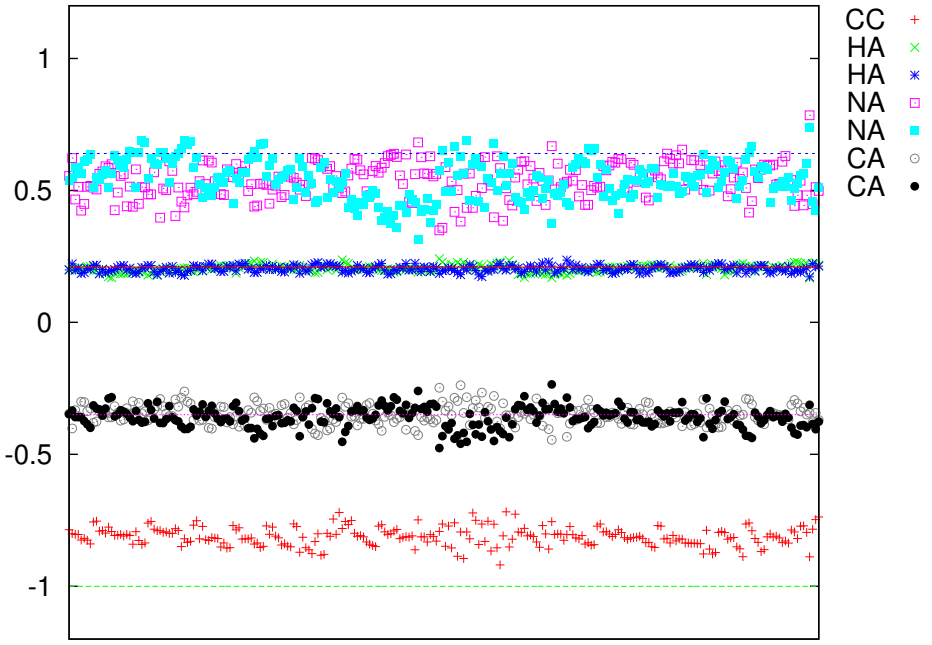

Figure 10: Partial Atomic Charges for **1** with different R in different conformations. The lines serve as guides to the eye and mark the partial atomic charges fitted in the force field.

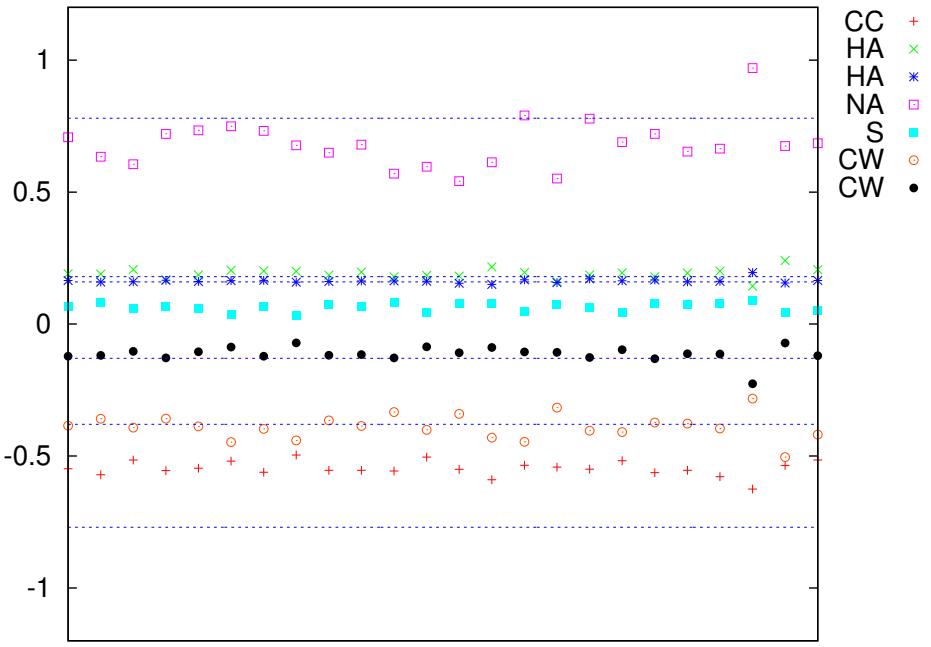

Figure 11: Partial Atomic Charges for **2** with different R in different conformations.

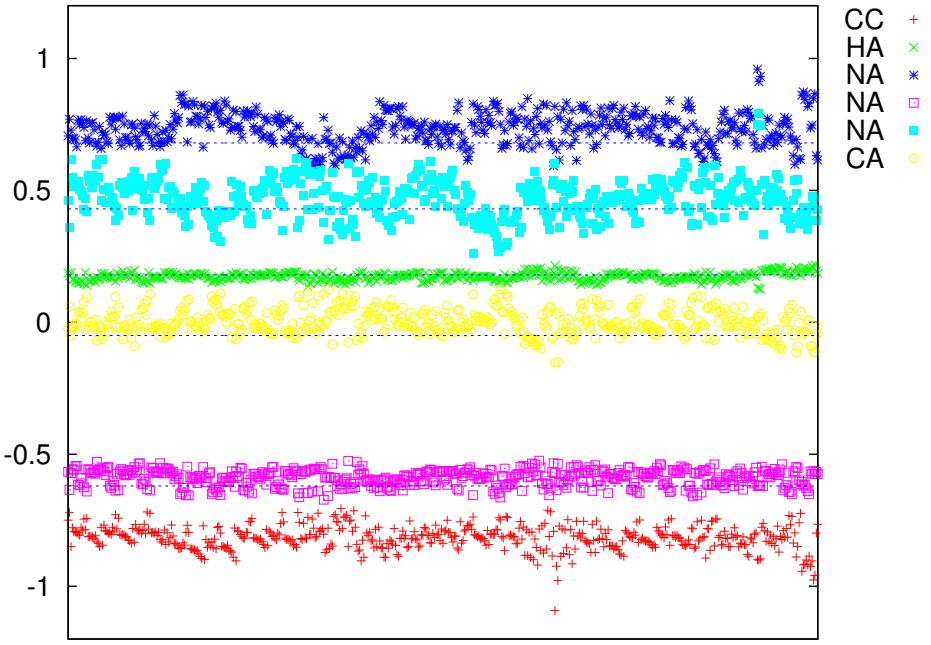

Figure 12: Partial Atomic Charges for **3** with different R in different conformations.

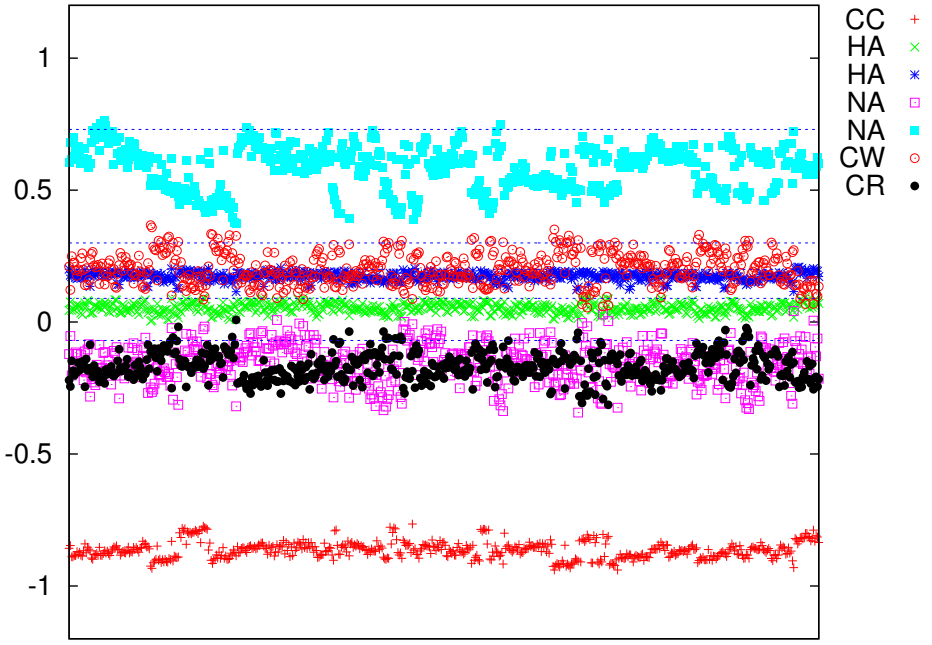

Figure 13: Partial Atomic Charges for **4** with different R in different conformations.

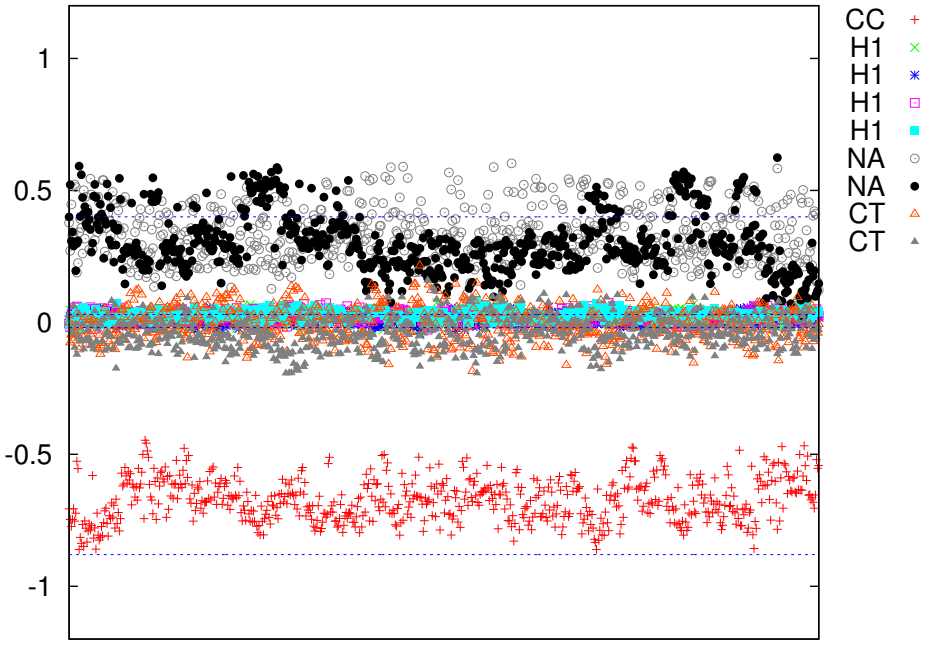

Figure 14: Partial Atomic Charges for **5** with different R in different conformations.

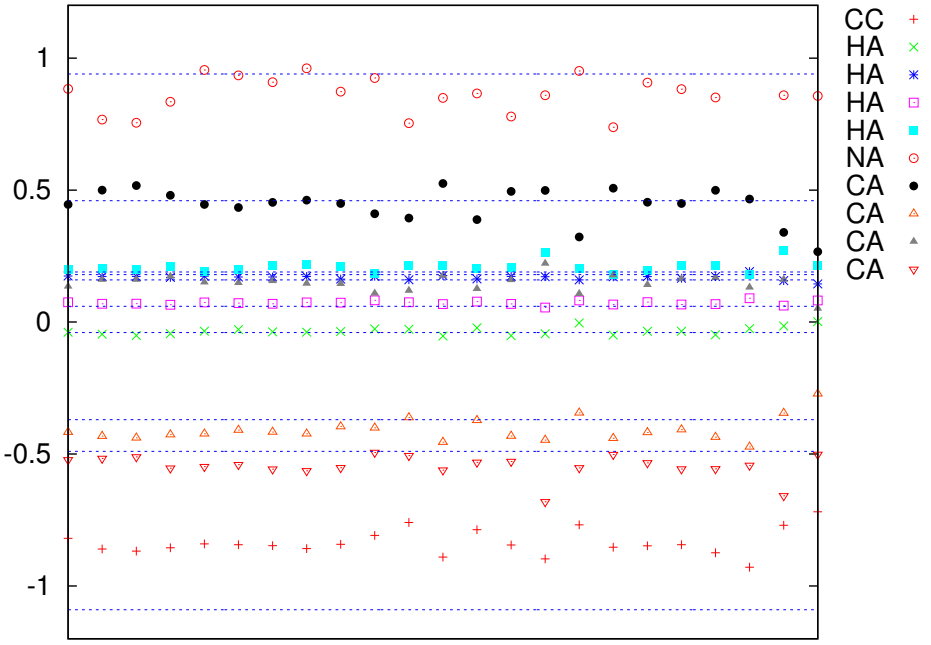

Figure 15: Partial Atomic Charges for **6** with different R in different conformations.

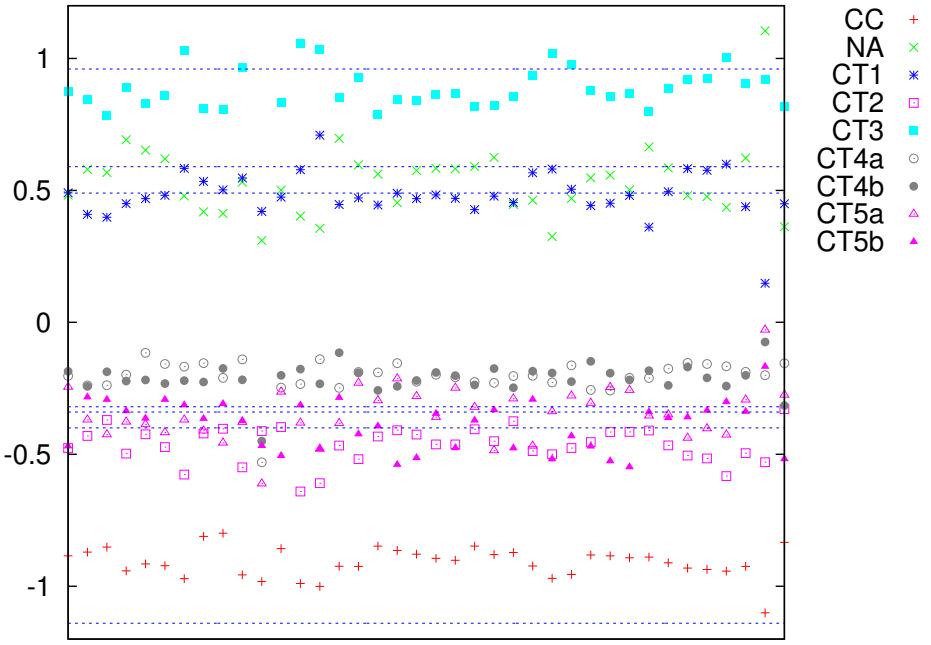

Figure 16: Partial Atomic Charges for **7** with different R in different conformations.

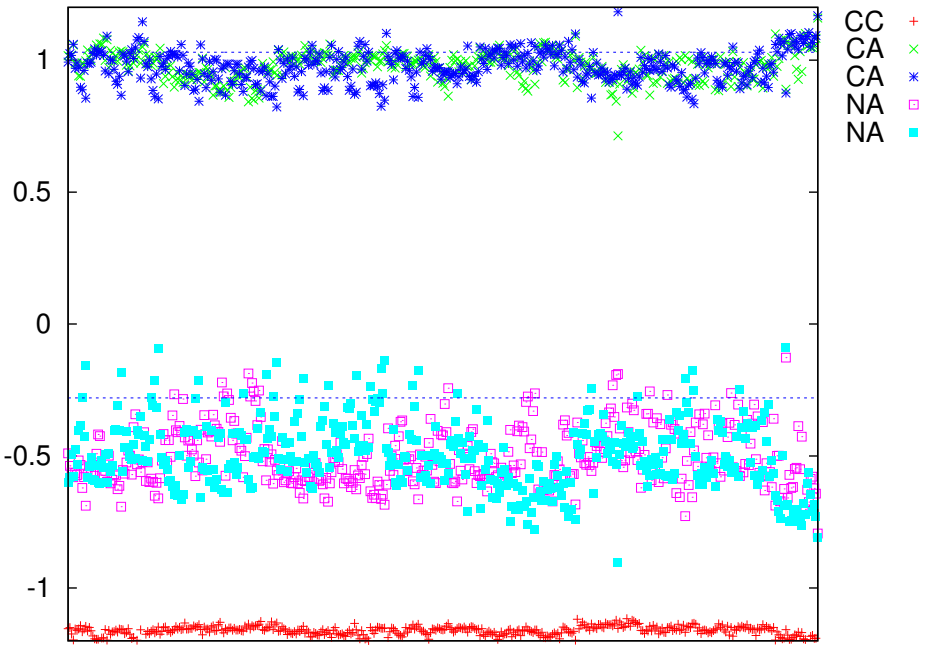

Figure 17: Partial Atomic Charges for **8** with different R in different conformations.

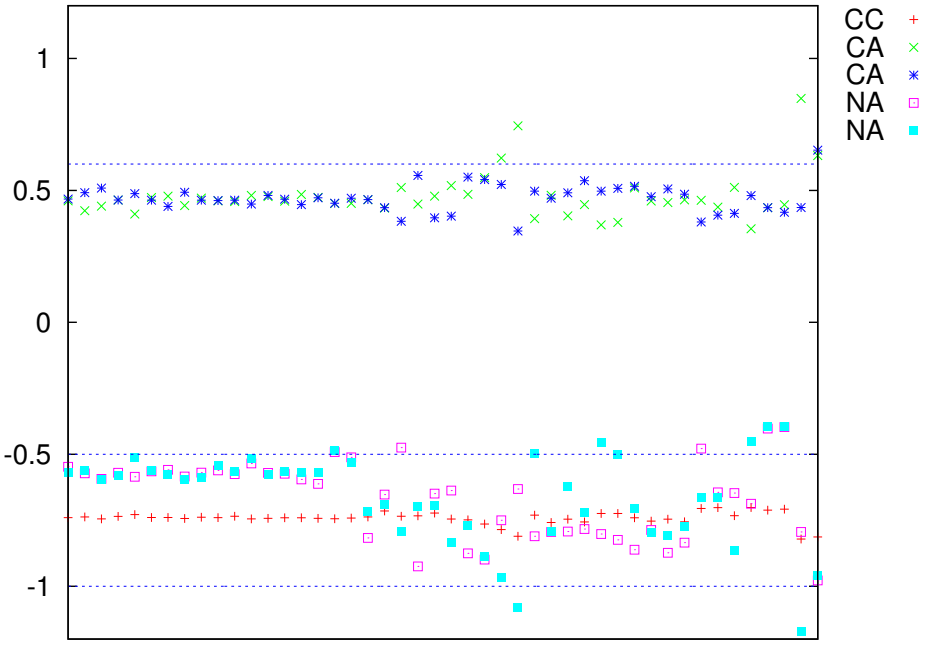

Figure 18: Partial Atomic Charges for **9** with different R in different conformations.

6 Thermodynamic Data for THF/Carbene-Mixtures

Table 40: Thermodynamic data calculated for pure THF and THF with an additive of 10 mol% of different carbenes.

Mixture	Viscosity in mPa · s	Heat capacity in J· mol^{-1}· K^{-1}	Diffusion coefficient in pm^2· ps^{-1}
pure THF	0.554	152	–
THF + Dimethylimidazol-2-ylidenes	0.650	157	1038
THF + Bisisopropylimidazol-2-ylidenes	1.059	202	92
THF + Methylthiazol-2-ylidenes	0.634	148	1352
exp.	0.456	123	–

7 Sum of Partial Atomic Charges on the Ring Atoms

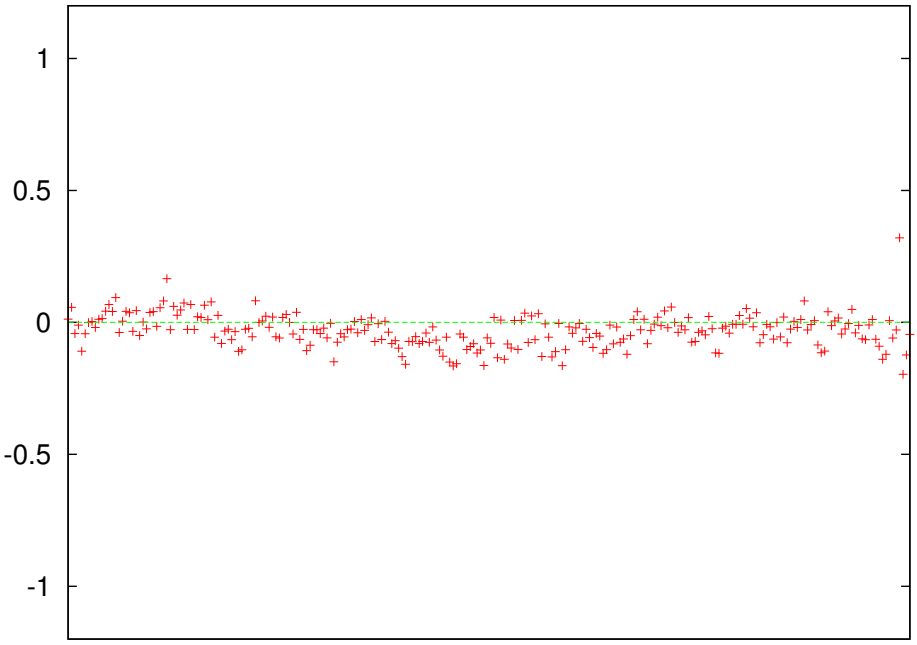

Figure 19: Sum of the partial atomic charges on atoms CC/L, NA, CA, HA of **1** with different R in different conformations. The line serves as a guide to the eye and marks the charge of the unit in the force field.

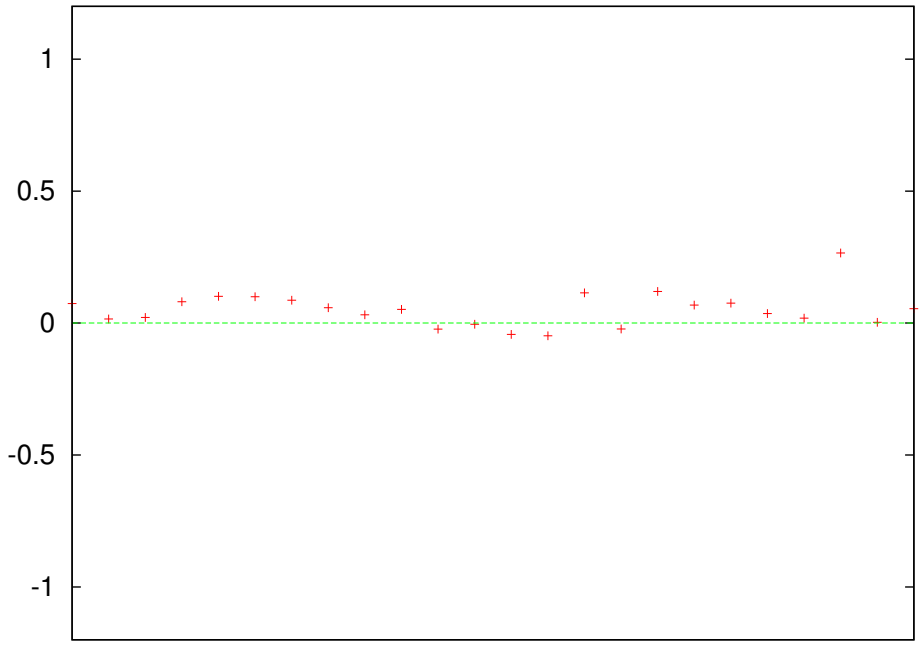

Figure 20: Sum of the partial atomic charges on atoms CC/L, NA, S, CW, HA of **2** with different R in different conformations. The line serves as a guide to the eye and marks the charge of the unit in the force field.

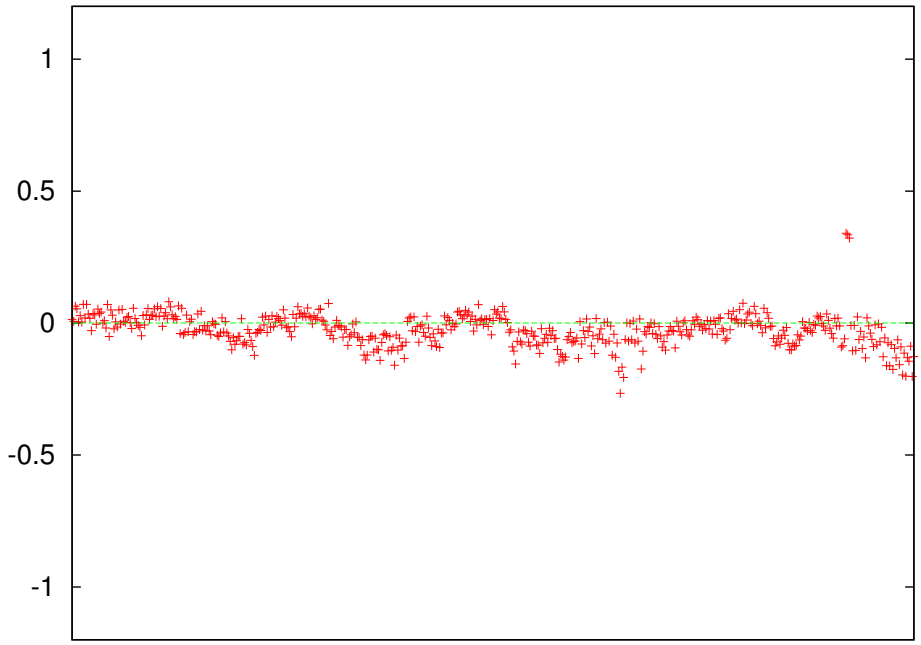

Figure 21: Sum of the partial atomic charges on atoms CC/L, NA, CR, HA of **3** with different R in different conformations. The line serves as a guide to the eye and marks the charge of the unit in the force field.

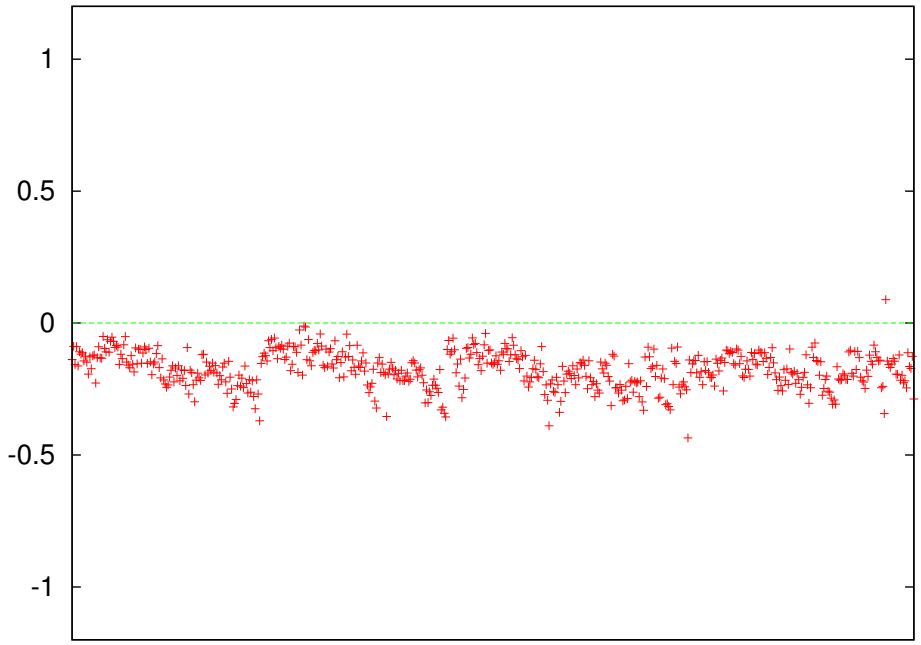

Figure 22: Sum of the partial atomic charges on atoms CC/L, NA, CW, CR, HA of **4** with different R in different conformations. The line serves as a guide to the eye and marks the charge of the unit in the force field.

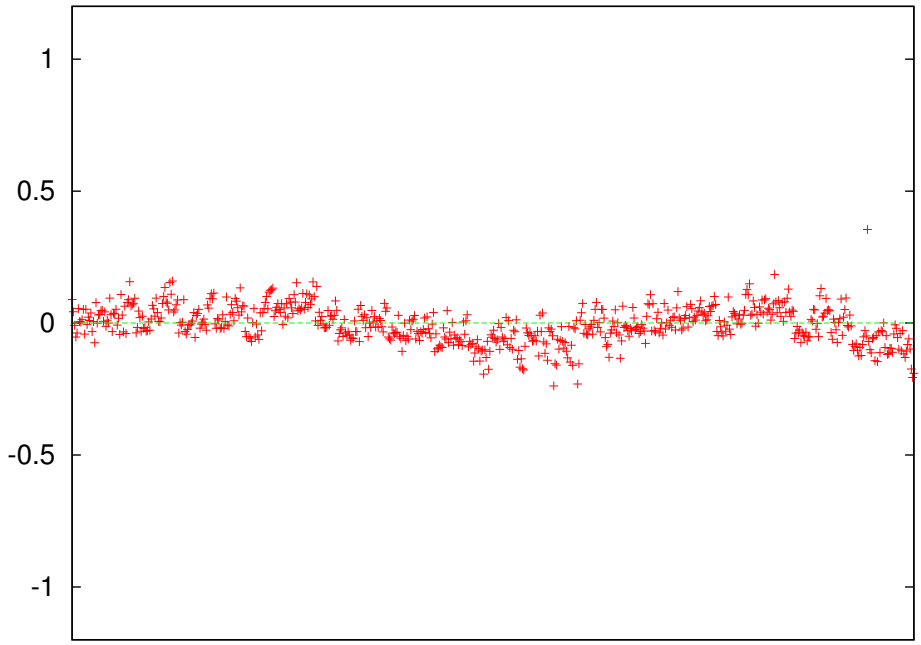

Figure 23: Sum of the partial atomic charges on atoms CC/L, NA, CT_{ring}, $H1_{ring}$ of **5** with different R in different conformations. The line serves as a guide to the eye and marks the charge of the unit in the force field.

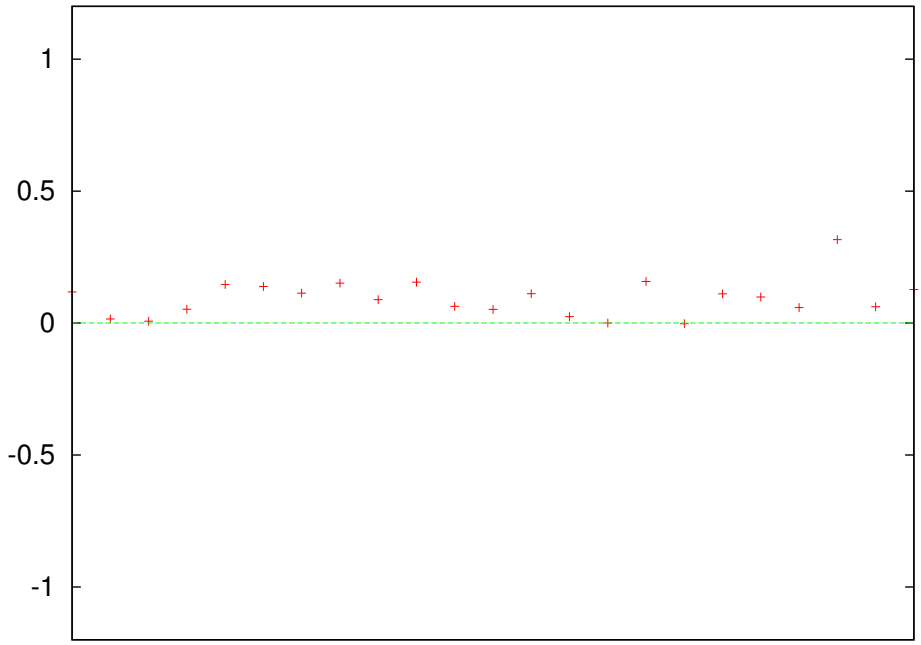

Figure 24: Sum of the partial atomic charges on atoms CC/L, NA, CA, HA of **6** with different R in different conformations. The line serves as a guide to the eye and marks the charge of the unit in the force field.

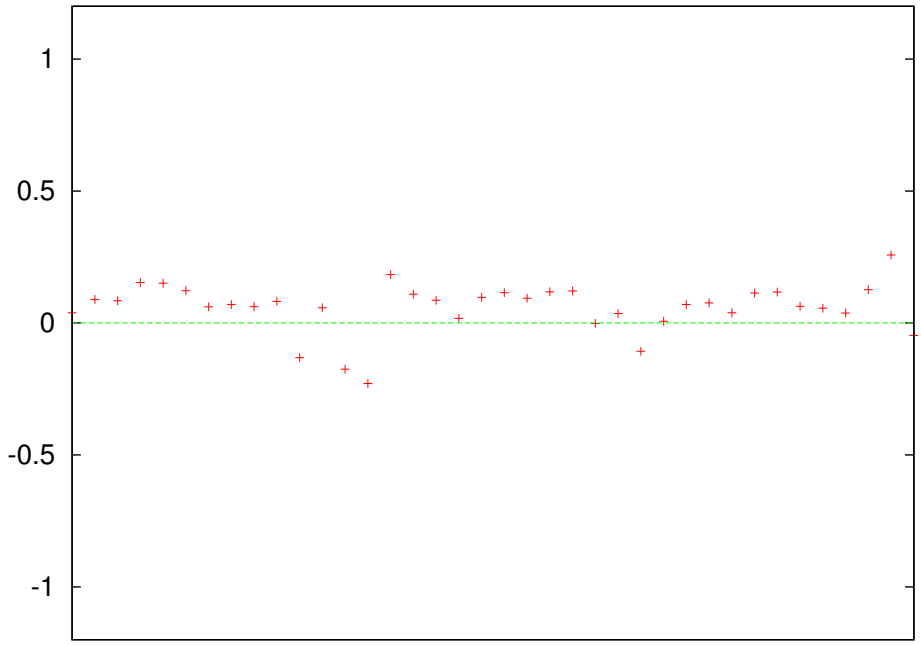

Figure 25: Sum of the partial atomic charges on atoms CC/L, NA, CT_{ring}, HC_{ring}, and the methylgroups bonded on the ring of **7** with different R in different conformations. The line serves as a guide to the eye and marks the charge of the unit in the force field.

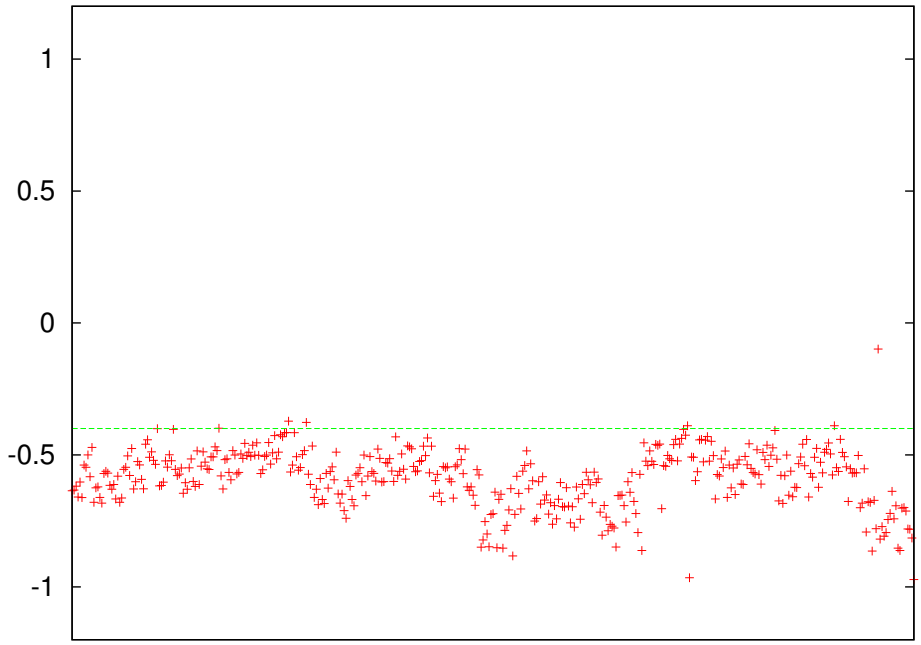

Figure 26: Sum of the partial atomic charges on atoms CC/L, CA, NA, and the methoxy groups bonded on the ring of **8** with different R in different conformations. The line serves as a guide to the eye and marks the charge of the unit in the force field.

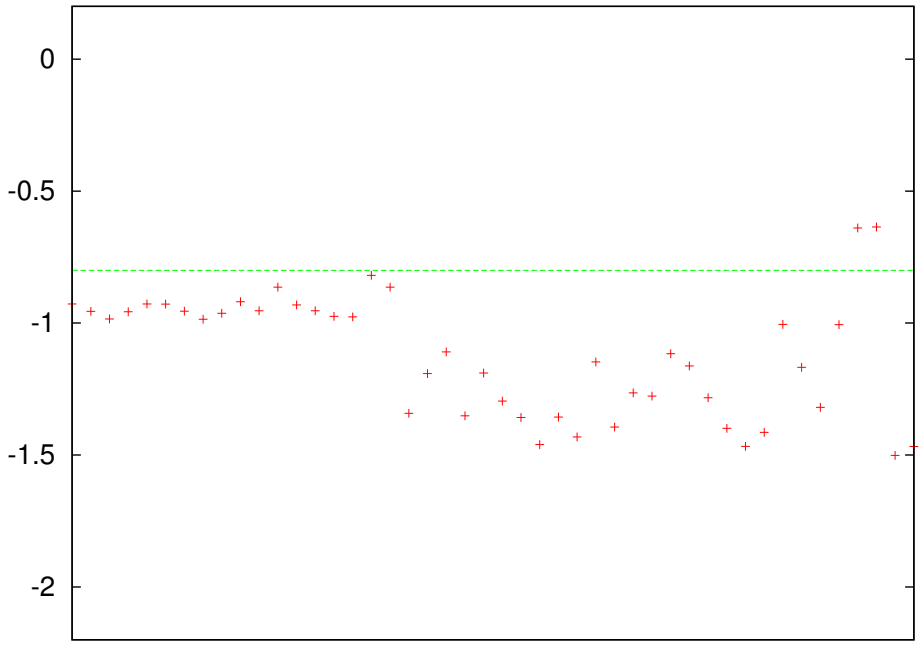

Figure 27: Sum of the partial atomic charges on atoms CC/L, CA, NA of **9** with different R in different conformations. The line serves as a guide to the eye and marks the charge of the unit in the force field.