Supplementary Material for PCCP

Supplementary Information for the article: Carbon and proton shielding tensors in methyl halides

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The molecular geometries used in theoretical computations and experimental analysis are shown in Table S1. Table S2 lists the theoretically computed temperature derivatives of ^{13}C and ^{1}H shielding constants and anisotropies. In Table S3, the dependence of nonrelativistic (NR) and relativistic (BPPT) results on the electron correlation treatment is shown. The breakdown of the BPPT(RAS) results for σ and $\Delta\sigma$ into the individual contributions is presented in Tables S4 and S5 for all methyl halides at their r_e geometries. The corresponding r_e data as well as the rovibrational corrections to each individual contribution at a given temperature at the MP2 and DFT(B3LYP) levels of theory, are presented in Tables S6 – S9. Eqs. (S1) and (S2) express the rovibrational averages of ^{13}C and ^{1}H shielding parameters. The displacement averages at $T = 300$ K of the molecular symmetry coordinates in those equations are listed for each methyl halide in Table S10. Finally, the rovibrational contributions at $T = 300$ K for each shielding parameter are shown in Tables S11 – S14.

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Table S1: Molecular geometries. [a]

Molecule	Geo[b]	r_{C-X}	r_{C-H}	∠XCH
CH_3F	r_e	1.383	1.0860	108.80
	r_α	1.391	1.0979	108.81
CH_3Cl	r_e	1.776	1.0854	108.58
	r_α	1.786	1.0944	108.43
CH_3Br	r_e	1.934	1.0823	107.73
	r_α	1.943	1.0930	107.69
CH_3I	r_e	2.132	1.0840	107.68
	r_α	2.142	1.0939	107.66

[a]Type of molecular geometry either r_e for equilibrium geometry or $r_\alpha(300\ \mathrm{K})$ for geometry where the nuclei are in their average locations corresponding to the temperature of 300 K. The geometries used are the same as in Refs. 1 (r_e) and 2 ($r_\alpha(300\ \mathrm{K})$). $^{13}C^1H_3X$ isotopomers with X=^{19}F, ^{35}Cl, ^{79}Br, and ^{127}I.

Table S2: Quantum-chemically calculated temperature derivatives (in ppb/K) of the ^{1}H and ^{13}C shielding constants and anisotropies in gas phase at the combined nonrelativistic MP2 and relativistic DFT(B3LYP) levels.[a]

Molecule	σ_C	$\Delta\sigma_C$	σ_H	$\Delta\sigma_H$
CH_3F	-0.715	0.553	-0.054	-0.028
CH_3Cl	-1.028	0.631	-0.059	-0.054
CH_3Br	-1.024	0.376	-0.050	-0.036
CH_3I	-0.481	-0.774	-0.065	-0.101

[a] Derivatives are calculated in the temperature range from 280 K to 350 K for the isotopomers $CH_3{}^{19}F$, $CH_3{}^{35}Cl$, $CH_3{}^{79}Br$, and $CH_3{}^{127}I$.

Table S3: Calculated nonrelativistic (NR) shielding constants (σ) and anisotropies ($\Delta\sigma$) with respect to the molecular C_3 axis in CH_3X (X = F – I). Relativistic BPPT corrections are also indicated.[a]

			σ				$\Delta\sigma$			
Nucleus	Term	Method	CH_3F	CH_3Cl	CH_3Br	CH_3I	CH_3F	CH_3Cl	CH_3Br	CH_3I
C	NR	HF	124.61	164.52	173.31	194.51	95.05	45.25	36.90	10.89
		MP2	121.42	167.17	177.94	200.19	107.84	49.29	38.10	10.60
		CCSD	123.61	167.25	177.51	198.83	101.98	46.23	35.72	9.46
		CCSD(T)	122.90	167.17	177.63	199.01	103.41	46.72	35.94	9.63
		RAS	125.43	168.18	178.28	199.55	100.35	46.28	37.01	9.80
		B3LYP	105.94	150.93	160.22	182.19	111.34	53.66	44.68	17.51
		BHandHLYP	113.36	156.53	165.64	187.43	105.43	50.62	41.85	14.91
	BPPT	RAS	1.24	2.88	10.30	28.96	-0.32	-2.86	-14.57	-43.93
		B3LYP	1.33	3.38	13.50	36.97	-0.44	-3.61	-19.39	-56.31
		BHandHLYP	1.31	3.27	12.79	35.48	-0.42	-3.45	-18.34	-54.01
H	NR	HF	27.98	29.09	29.33	29.92	4.08	4.75	5.94	7.27
		MP2	27.40	28.67	28.98	29.60	4.60	4.99	6.14	7.45
		CCSD	27.60	28.88	29.17	29.79	4.42	4.86	6.04	7.35
		CCSD(T)	27.50	28.79	29.09	29.71	4.53	4.95	6.13	7.44
		RAS	27.74	28.87	29.16	29.81	4.23	4.81	5.91	7.27
		B3LYP	27.44	28.73	29.04	29.67	5.08	5.51	6.67	7.93
		BHandHLYP	27.62	28.83	29.11	29.73	4.62	5.16	6.32	7.61
	BPPT	RAS	0.03	0.03	0.03	-0.38	-0.01	0.00	0.12	0.79
		B3LYP	0.03	0.04	0.07	-0.28	0.00	-0.01	0.15	0.83
		BHandHLYP	0.03	0.04	0.07	-0.33	-0.01	-0.01	0.13	0.86

[a] Results in ppm at the equilibrium geometry (see text). The HIV(C,H)/FIV(X) basis is used.

Table S4: Ab initio nonrelativistic (NR) and relativistic (BPPT) contributions to ^{13}C shielding constants (σ) and anisotropies ($\Delta\sigma$) in CH_3X (X = H, F, Cl, Br, I) at the equilibrium geometry.[a]

	σ_C					$\Delta\sigma_C$			
Term	CH_4	CH_3F	CH_3Cl	CH_3Br	CH_3I	CH_3F	CH_3Cl	CH_3Br	CH_3I
NR	199.19	122.90	167.17	177.63	199.01	103.41	46.72	35.94	9.63
con	-0.74	-0.74	-0.74	-0.74	-0.74	–	–	–	–
dip	–	–	–	–	–	0.00	0.00	0.00	0.00
d-KE	-0.56	-0.55	-0.55	-0.55	-0.55	-0.02	-0.02	-0.02	-0.02
p-OZ	-0.01	0.00	0.00	0.00	0.00	-0.01	-0.01	-0.02	-0.01
d/mv	0.96	0.97	0.99	1.06	1.16	-0.02	-0.07	-0.33	-0.74
d/Dar	-0.58	-0.60	-0.62	-0.69	-0.79	0.02	0.05	0.17	0.36
p/OZ-KE	0.03	0.01	0.01	0.01	0.01	0.04	0.04	0.04	0.03
p-KE/OZ	0.08	0.11	0.08	0.07	0.06	-0.04	0.00	0.01	0.04
FC/SZ-KE	2.53	2.52	2.52	2.52	2.52	–	–	–	–
SD/SZ-KE	–	–	–	–	–	-0.01	-0.01	-0.01	-0.01
FC-II(1)	-0.45	-0.45	-0.45	-0.45	-0.44	0.02	0.02	0.03	0.04
SD-II(1)	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01
p/mv	-0.05	-0.30	-0.49	-1.98	-5.38	0.31	0.57	2.70	7.57
p/Dar	-0.04	0.05	0.11	0.31	1.08	-0.14	-0.20	-0.44	-1.51
FC-I(1)	-0.03	0.54	2.78	13.14	38.18	-0.90	-4.31	-20.06	-57.85
SD-I(1)	-0.03	-0.03	-0.13	-0.85	-3.28	0.04	0.16	1.02	3.89
FC-I(2)	-0.03	-0.29	-0.67	-1.65	-3.09	0.40	0.97	2.46	4.62
SD-I(2)	0.01	0.00	0.03	0.11	0.27	-0.02	-0.04	-0.14	-0.31
TOTAL(SR)[d]	-0.92	-1.05	-1.21	-2.51	-5.15	0.15	0.35	2.12	5.70
TOTAL(SO)[e]	2.01	2.29	4.09	12.81	34.16	-0.46	-3.21	-16.69	-49.61
BPPT-5[f]	-0.10	0.08	1.71	9.13	27.83	-0.34	-2.85	-14.44	-43.56
BPPT[g]	1.09	1.24	2.88	10.30	29.00	-0.32	-2.86	-14.57	-43.91
TOTAL[h]	200.28	122.98	168.88	186.76	226.85	103.09	43.86	21.37	-34.28

[a] NR terms computed at CCSD(T) level with HIV(C,H)/FIV(X) basis set. BPPT contributions were computed at RAS level with HIVu2(C,H)/FIV(X) basis set.
[b] Computed with HIV(C,H)/FIV(X) basis set.
[c] Two-electron terms computed at DFT(B3LYP) level with HIVu2(C,H)/FIV(X) basis set.
[d] Sum of all electron-spin-independent BPPT terms.
[e] Sum of all electron-spin-dependent BPPT terms.
[f] Sum of terms [*p*-KE/OZ, *p*/mv, *p*/Dar, FC-I(1&2), and SD-I(1&2)], which have been found the most important for heavy-atom δ and $\Delta\sigma$.
[g] TOTAL(SR)+TOTAL(SO).
[h] NR+BPPT.

Table S5: Ab initio nonrelativistic (NR) and relativistic (BPPT) contributions to ^{1}H shielding constants (σ) and anisotropies ($\Delta\sigma$) in CH_3X (X = H, F, Cl, Br, I) at the equilibrium geometry.[a]

	σ_H					$\Delta\sigma_H$			
Term	CH_4	CH_3F	CH_3Cl	CH_3Br	CH_3I	CH_3F	CH_3Cl	CH_3Br	CH_3I
NR	31.46	27.50	28.79	29.09	29.71	4.53	4.95	6.13	7.44
con	0.00	0.00	0.00	0.00	0.00	–	–	–	–
dip	–	–	–	–	–	0.00	0.00	0.00	0.00
d-KE	0.00	0.01	0.01	0.01	0.01	-0.01	-0.01	-0.02	-0.02
p-OZ	0.00	0.01	0.01	0.01	0.01	-0.01	-0.01	-0.01	-0.01
d/mv	0.00	0.00	0.01	0.05	0.11	0.01	0.00	-0.06	-0.21
d/Dar	0.00	0.00	-0.01	-0.06	-0.12	-0.01	0.00	0.01	0.07
p/OZ-KE	0.00	-0.01	-0.02	-0.02	-0.02	0.02	0.02	0.02	0.03
p-KE/OZ	0.00	-0.01	-0.02	-0.02	-0.02	0.02	0.02	0.02	0.02
FC/SZ-KE	0.00	0.00	0.00	0.00	0.00	–	–	–	–
SD/SZ-KE	–	–	–	–	–	0.00	0.00	0.00	0.00
FC-II(1)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SD-II(1)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
p/mv	-0.01	0.00	0.00	-0.04	-0.11	-0.01	-0.01	0.01	0.10
p/Dar	0.00	0.01	0.01	0.03	0.06	0.00	0.00	0.00	-0.02
FC-I(1)	0.02	0.05	0.05	0.04	-0.36	-0.01	0.02	0.14	0.85
SD-I(1)	0.00	0.00	0.01	0.03	0.05	0.00	0.01	0.03	0.07
FC-I(2)[c]	-0.01	-0.01	-0.01	-0.01	0.02	-0.01	-0.02	-0.04	-0.08
SD-I(2)[c]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	-0.01
TOTAL(SR)[d]	-0.01	-0.01	-0.01	-0.03	-0.09	0.00	0.00	-0.02	-0.04
TOTAL(SO)[e]	0.01	0.04	0.04	0.06	-0.29	-0.02	0.00	0.13	0.83
BPPT-5[f]	0.01	0.03	0.04	0.04	-0.36	-0.02	0.01	0.17	0.94
BPPT[g]	0.00	0.03	0.03	0.03	-0.38	-0.01	0.00	0.12	0.79
TOTAL[h]	31.46	27.53	28.82	29.12	29.32	4.52	4.96	6.25	8.24

[a] See footnotes in Table S4.

Table S6: Nonrelativistic (NR) and relativistic (BPPT) terms as well as their rovibrational corrections (at 300 K and/or 350 K) at the DFT(B3LYP) level for the ^{13}C shielding constant, σ_C in CH_3X (X = F – I).[a]

	CH_3F		CH_3Cl		CH_3Br		CH_3I		
	r_e	300 K	r_e	300 K	r_e	300 K	r_e	300 K	350 K
NR[b]	104.89	-4.78	150.14	-4.03	159.48	-4.11	182.19	-3.47	-3.55
	(121.42)	(-3.81)	(167.17)	(-2.86)	(177.94)	(-2.78)	(200.18)	(-2.14)	(-2.20)
con	-0.74	0.00	-0.74	0.00	-0.74	0.00	-0.74	0.00	0.00
d-KE	-0.55	0.00	-0.56	0.00	-0.56	0.00	-0.56	0.00	0.00
p-OZ	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
d/mv	0.98	0.00	1.00	0.00	1.08	0.00	1.20	0.00	0.00
d/Dar	-0.60	0.00	-0.62	0.00	-0.70	0.00	-0.81	0.00	0.00
p/OZ-KE	0.01	0.00	0.01	0.00	0.01	0.00	0.02	0.00	0.00
p-KE/OZ	0.14	0.00	0.10	0.00	0.10	0.00	0.08	0.00	0.00
FC/SZ-KE	2.53	0.00	2.54	0.00	2.54	0.00	2.54	0.00	0.00
FC-II(1)	-0.45	0.00	-0.45	0.00	-0.45	0.00	-0.45	0.00	0.00
SD-II(1)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
p/mv	-0.39	-0.01	-0.61	-0.02	-2.18	-0.09	-5.39	-0.19	-0.17
p/Dar	0.07	0.00	0.14	0.00	0.35	0.04	0.86	0.09	0.08
FC-I(1)	0.66	0.03	3.35	0.16	16.64	1.01	46.99	3.27	3.33
SD-I(1)	-0.04	0.00	-0.15	-0.01	-1.05	-0.04	-3.95	-0.17	-0.19
FC-I(2)	-0.29	-0.01	-0.67	-0.03	-1.65	-0.10	-3.09	-0.21	-0.22
SD-I(2)	0.00	0.00	0.03	0.00	0.11	0.00	0.27	0.01	0.01
BPPT	1.33	0.01	3.38	0.12	13.50	0.83	36.97	2.82	2.85
TOTAL[c]	106.22	-4.77	153.52	-3.91	172.97	-3.28	219.16	-0.65	-0.69
		(-3.80)		(-2.74)		(-1.95)		(0.68)	(0.66)

[a] r_e denotes calculation with HIVu2(C,H)/FIV(X) basis set at equilibrium geometry. The numbers under the columns denoted 300 K and 350 K are rovibrational contributions to be added to the equilibrium value, at the indicated temperature for the isotopomers $CH_3{}^{19}F$, $CH_3{}^{35}Cl$, $CH_3{}^{79}Br$, and $CH_3{}^{127}I$. BPPT is a sum of the all BPPT terms.
[b] The NR results at the MP2 level with HIV(C,H)/FIV(X) basis are in parentheses.
[c] TOTAL = NR + BPPT at the DFT(B3LYP) level. In parentheses the total rovibrational averages as a sum of NR(MP2) and BPPT(DFT/B3LYP) rovibrational corrections, used for the best results of the article.

Table S7: Nonrelativistic (NR) and relativistic (BPPT) terms as well as their rovibrational corrections (at 300 K and/or 350 K) at the DFT(B3LYP) level for the ^{13}C shielding anisotropy, $\Delta\sigma_C$ in CH_3X (X = F – I).[a]

	CH_3F		CH_3Cl		CH_3Br		CH_3I		
	r_e	300 K	r_e	300 K	r_e	300 K	r_e	300 K	350 K
NR	111.89	-0.08	53.87	-1.19	44.83	-2.01	17.51	-2.91	-2.88
	(107.84)	(-0.01)	(49.29)	(-1.17)	(38.10)	(-1.94)	(10.60)	(-2.81)	(-2.79)
dip	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
d-KE	-0.02	0.00	-0.02	0.00	-0.02	0.00	-0.02	0.00	0.00
p-OZ	-0.01	0.00	-0.01	0.00	-0.01	0.00	-0.01	0.00	0.00
d/mv	-0.02	0.00	-0.07	0.00	-0.32	0.00	-0.75	0.01	0.01
d/Dar	0.02	0.00	0.05	0.00	0.16	0.00	0.36	0.00	0.00
p/OZ-KE	0.04	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.00
p-KE/OZ	-0.06	0.00	-0.01	0.00	0.00	0.00	0.03	0.00	0.00
SD/SZ-KE	-0.01	0.00	-0.01	0.00	-0.01	0.00	-0.01	0.00	0.00
FC-II(1)	0.02	0.00	0.02	0.00	0.03	0.00	0.04	0.00	0.00
SD-II(1)	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00
p/mv	0.40	0.00	0.68	0.00	2.93	0.05	7.46	0.10	0.07
p/Dar	-0.18	0.00	-0.25	0.00	-0.49	-0.03	-1.16	-0.07	-0.05
FC-I(1)	-1.07	-0.04	-5.16	-0.23	-25.29	-1.40	-71.06	-4.57	-4.65
SD-I(1)	0.05	0.01	0.20	0.02	1.27	0.11	4.46	0.33	0.35
FC-I(2)	0.40	0.02	0.97	0.04	2.46	0.14	4.62	0.30	0.30
SD-I(2)	-0.02	0.00	-0.04	0.00	-0.14	-0.01	-0.31	-0.02	-0.02
BPPT	-0.44	-0.02	-3.61	-0.17	-19.39	-1.15	-56.31	-3.93	-3.99
TOTAL	111.45	-0.10	50.26	-1.35	25.44	-3.15	-38.80	-6.84	-6.87
		(-0.03)		(-1.37)		(-3.09)		(-6.74)	(-6.78)

[a] See footnotes in Table S6.

Table S8: Nonrelativistic (NR) and relativistic (BPPT) terms as well as their rovibrational corrections (at 300 K and/or 350 K) at the DFT(B3LYP) level for the ^{1}H shielding constant, σ_{H} in CH_3X ($X = \mathrm{F} - \mathrm{I}$).[a]

	CH_3F		CH_3Cl		CH_3Br		CH_3I		
	r_e	300 K	r_e	300 K	r_e	300 K	r_e	300 K	350 K
NR	27.45	-0.63	28.73	-0.59	29.04	-0.63	29.67	-0.60	-0.60
	(27.40)	(-0.63)	(28.67)	(-0.58)	(28.98)	(-0.62)	(29.59)	(-0.59)	(-0.59)
con	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
d-KE	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00
p-OZ	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00
d/mv	0.00	0.00	0.01	0.00	0.05	0.00	0.11	0.01	0.01
d/Dar	0.00	0.00	-0.01	0.00	-0.06	0.00	-0.12	0.00	0.00
p/OZ-KE	-0.01	0.00	-0.02	0.00	-0.02	0.00	-0.02	0.00	0.00
p-KE/OZ	-0.01	0.00	-0.02	0.00	-0.02	0.00	-0.02	0.00	0.00
FC/SZ-KE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FC-II(1)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SD-II(1)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
p/mv	-0.01	0.00	-0.01	0.00	-0.05	0.00	-0.12	0.00	0.00
p/Dar	0.02	0.00	0.02	0.00	0.04	0.00	0.06	0.00	0.00
FC-I(1)	0.05	0.01	0.06	0.01	0.09	0.04	-0.26	0.03	0.03
SD-I(1)	0.00	0.00	0.01	0.00	0.03	0.00	0.06	0.01	0.01
FC-I(2)	-0.01	0.00	-0.01	0.00	-0.01	0.00	0.02	0.00	0.00
SD-I(2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BPPT	0.03	0.00	0.04	0.01	0.07	0.04	-0.28	0.04	0.03
TOTAL	27.47	-0.63	28.77	-0.57	29.12	-0.59	29.39	-0.56	-0.57
		(-0.63)		(-0.56)		(-0.58)		(-0.55)	(-0.56)

[a] See footnotes in Table S6.

Table S9: Nonrelativistic (NR) and relativistic (BPPT) terms as well as their rovibrational corrections (at 300 K and/or 350 K) at the DFT(B3LYP) level for the ^{1}H shielding anisotropy, $\Delta\sigma_{\mathrm{H}}$ in CH_3X (X = F – I).[a]

	CH_3F		CH_3Cl		CH_3Br		CH_3I		
	r_e	300 K	r_e	300 K	r_e	300 K	r_e	300 K	350 K
NR	5.08	-0.03	5.51	-0.04	6.67	-0.09	7.93	-0.13	-0.13
	(4.60)	(-0.05)	(4.99)	(-0.06)	(6.14)	(-0.03)	(7.45)	(-0.16)	(-0.17)
dip	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
d-KE	-0.01	0.00	-0.01	0.00	-0.02	0.00	-0.02	0.00	0.00
p-OZ	-0.01	0.00	-0.01	0.00	-0.01	0.00	-0.01	0.00	0.00
d/mv	0.01	0.00	0.00	0.00	-0.05	0.00	-0.17	0.00	0.00
d/Dar	-0.01	0.00	0.00	0.00	0.01	0.00	0.04	0.00	0.00
p/OZ-KE	0.02	0.00	0.02	0.00	0.02	0.00	0.03	0.00	0.00
p-KE/OZ	0.02	0.00	0.02	0.00	0.02	0.00	0.02	0.00	0.00
SD/SZ-KE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FC-II(1)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SD-II(1)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
p/mv	-0.01	0.00	-0.01	0.00	0.03	0.00	0.09	-0.01	-0.01
p/Dar	-0.01	0.00	-0.01	0.00	-0.01	0.00	-0.02	0.01	0.01
FC-I(1)	0.00	0.00	0.03	0.00	0.15	0.00	0.85	0.04	0.05
SD-I(1)	0.01	0.00	0.01	0.00	0.05	0.00	0.10	-0.01	-0.01
FC-I(2)	-0.01	0.00	-0.02	0.00	-0.04	0.00	-0.08	0.00	-0.01
SD-I(2)	0.00	0.00	0.00	0.00	-0.01	0.00	-0.01	0.00	0.00
BPPT	0.00	0.00	0.02	0.00	0.15	-0.01	0.83	0.02	0.03
TOTAL	5.07	-0.03	5.54	-0.05	6.82	-0.10	8.76	-0.10	-0.11
		(-0.05)		(-0.07)		(-0.4)		(-0.13)	(-0.14)

[a] See footnotes in Table S6.

For ^{13}C in C_{3v} site symmetry the thermal averages of shielding parameters can be written as

$$\begin{aligned}\langle\sigma_{\mathrm{C}}\rangle^T &= \sigma_e + \overbrace{\sigma_1\langle S_1\rangle^T}^{=\langle\sigma_1\rangle^T} + \sigma_2\langle S_2\rangle^T + \sigma_3\langle S_3\rangle^T \\ &\quad + \frac{1}{2}\sigma_{11}\langle S_1S_1\rangle^T + \frac{1}{2}\sigma_{22}\langle S_2S_2\rangle^T + \frac{1}{2}\sigma_{33}\langle S_3S_3\rangle^T \\ &\quad + \sigma_{12}\langle S_1S_2\rangle^T + \sigma_{13}\langle S_1S_3\rangle^T + \sigma_{23}\langle S_2S_3\rangle^T \\ &\quad + \sigma_{44}\langle S_4S_4\rangle^T + \sigma_{55}\langle S_5S_5\rangle^T + \sigma_{66}\langle S_6S_6\rangle^T \\ &\quad + 2\sigma_{45}\langle S_4S_5\rangle^T + 2\sigma_{46}\langle S_4S_6\rangle^T + \underbrace{2\sigma_{56}\langle S_5S_6\rangle^T}_{=\langle\sigma_{56}\rangle^T}\end{aligned} \tag{S1}$$

and for ^{1}H in C_s site symmetry the thermal averages of shielding parameters are

$$\begin{aligned}\langle\sigma_{\mathrm{H}}\rangle^T &= \sigma_e + \overbrace{\sigma_1\langle S_1\rangle^T}^{=\langle\sigma_1\rangle^T} + \sigma_2\langle S_2\rangle^T + \sigma_3\langle S_3\rangle^T \\ &\quad + \frac{1}{2}\sigma_{11}\langle S_1S_1\rangle^T + \frac{1}{2}\sigma_{22}\langle S_2S_2\rangle^T + \frac{1}{2}\sigma_{33}\langle S_3S_3\rangle^T \\ &\quad + \frac{1}{2}\sigma_{4a4a}\langle S_4S_4\rangle^T + \frac{1}{2}\sigma_{5a5a}\langle S_5S_5\rangle^T + \frac{1}{2}\sigma_{6a6a}\langle S_6S_6\rangle^T \\ &\quad + \frac{1}{2}\sigma_{4b4b}\langle S_4S_4\rangle^T + \frac{1}{2}\sigma_{5b5b}\langle S_5S_5\rangle^T + \frac{1}{2}\sigma_{6b6b}\langle S_6S_6\rangle^T \\ &\quad + \sigma_{12}\langle S_1S_2\rangle^T + \sigma_{13}\langle S_1S_3\rangle^T + \sigma_{23}\langle S_2S_3\rangle^T \\ &\quad + \sigma_{4a5a}\langle S_4S_5\rangle^T + \sigma_{4a6a}\langle S_4S_6\rangle^T + \sigma_{5a6a}\langle S_5S_6\rangle^T \\ &\quad + \sigma_{4b5b}\langle S_4S_5\rangle^T + \sigma_{4b6b}\langle S_4S_6\rangle^T + \underbrace{\sigma_{5b6b}\langle S_5S_6\rangle^T}_{=\langle\sigma_{5b6b}\rangle^T}.\end{aligned} \tag{S2}$$

See, *e.g.*, Ref. 3 for the definitions of the symmetry coordinates S_i.

Table S10: Linear, $\langle S_i \rangle^T$ and quadratic, $\langle S_i S_j \rangle^T$, averages of molecular symmetry coordinates at $T = 300$ K in $^{13}CH_3X$ ($X = {}^{19}$F, ^{35}Cl, ^{79}Br, ^{127}I).[a]

	CH_3F	CH_3Cl	CH_3Br	CH_3I
$\langle S_1 \rangle^T$	0.0383	0.0353	0.0391	0.0388
$\langle S_2 \rangle^T$	-0.0033	0.0029	-0.0022	-0.0035
$\langle S_3 \rangle^T$	0.0090	0.0116	0.0111	0.0116
$\langle S_1 S_1 \rangle^T$	0.0057	0.0056	0.0055	0.0055
$\langle S_1 S_2 \rangle^T$	-0.0007	-0.0005	-0.0006	-0.0007
$\langle S_1 S_3 \rangle^T$	-0.0003	-0.0003	-0.0003	-0.0003
$\langle S_2 S_2 \rangle^T$	0.0227	0.0243	0.0247	0.0256
$\langle S_2 S_3 \rangle^T$	0.0022	0.0026	0.0028	0.0030
$\langle S_3 S_3 \rangle^T$	0.0021	0.0025	0.0026	0.0030
$\langle S_4 S_4 \rangle^T$	0.0118	0.0117	0.0117	0.0116
$\langle S_4 S_5 \rangle^T$	0.0019	0.0019	0.0020	0.0020
$\langle S_4 S_6 \rangle^T$	-0.0012	-0.0010	-0.0010	-0.0012
$\langle S_5 S_5 \rangle^T$	0.0524	0.0536	0.0546	0.0548
$\langle S_5 S_6 \rangle^T$	0.0049	0.0043	0.0043	0.0043
$\langle S_6 S_6 \rangle^T$	0.0276	0.0298	0.0315	0.0338

[a] $\langle S_m S_n \rangle^T = \langle S_{ma} S_{na} \rangle^T = \langle S_{mb} S_{nb} \rangle^T$ for $m, n = 4, 5, 6$. In Å and rad units.

Table S11: Computational rovibrational contributions to the ^{13}C nuclear shielding constant, $\langle\sigma_i\rangle^T$, at $T = 300$ K for CH_3X ($X = {}^{19}$F, ^{35}Cl, ^{79}Br, ^{127}I).[a]

	CH_3F		CH_3Cl		CH_3Br		CH_3I	
	NR	BPPT	NR	BPPT	NR	BPPT	NR	BPPT
$\langle\sigma_1\rangle^T$	-2.98	0.01	-3.02	0.08	-3.31	0.58	-3.21	1.85
$\langle\sigma_2\rangle^T$	0.05	0.00	0.01	0.00	-0.02	0.03	-0.06	0.15
$\langle\sigma_3\rangle^T$	-0.81	0.01	-1.11	0.03	-1.09	0.16	-1.16	0.42
$\langle\sigma_{11}\rangle^T$	-0.14	0.00	-0.20	0.00	-0.22	0.03	-0.24	0.12
$\langle\sigma_{12}\rangle^T$	0.00	0.00	0.00	0.00	-0.01	0.00	-0.01	0.01
$\langle\sigma_{13}\rangle^T$	-0.01	0.00	-0.02	0.00	-0.02	0.00	-0.02	-0.01
$\langle\sigma_{22}\rangle^T$	0.31	0.00	0.87	-0.01	1.04	-0.08	1.30	-0.22
$\langle\sigma_{23}\rangle^T$	0.03	0.00	-0.04	-0.02	-0.06	-0.13	-0.11	-0.39
$\langle\sigma_{33}\rangle^T$	-0.21	0.00	-0.18	0.01	-0.14	0.08	-0.10	0.25
$\langle\sigma_{44}\rangle^T$	-0.79	0.00	-0.89	-0.01	-0.91	-0.04	-0.93	-0.11
$\langle\sigma_{45}\rangle^T$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
$\langle\sigma_{46}\rangle^T$	0.00	0.00	0.03	0.00	0.05	0.00	0.08	0.01
$\langle\sigma_{55}\rangle^T$	0.82	0.00	1.05	-0.01	1.08	-0.05	1.19	-0.12
$\langle\sigma_{56}\rangle^T$	0.01	0.00	0.02	0.00	0.02	0.00	0.02	0.00
$\langle\sigma_{66}\rangle^T$	-0.11	0.00	0.61	0.04	0.80	0.25	1.12	0.86
Sum	-3.81	0.01	-2.86	0.12	-2.78	0.83	-2.14	2.82

[a] In ppm. See Eq. (S1).

Table S12: Computational rovibrational contributions to the ^{13}C nuclear shielding anisotropy, $\langle\Delta\sigma_i\rangle^T$, at $T = 300$ K for CH_3X ($X = {}^{19}$F, ^{35}Cl, ^{79}Br, ^{127}I).[a]

	CH_3F		CH_3Cl		CH_3Br		CH_3I	
	NR	BPPT	NR	BPPT	NR	BPPT	NR	BPPT
$\langle\Delta\sigma_1\rangle^T$	-2.28	-0.02	-1.65	-0.12	-1.84	-0.82	-1.85	-2.64
$\langle\Delta\sigma_2\rangle^T$	0.06	0.00	-0.12	0.01	0.11	-0.04	0.22	-0.21
$\langle\Delta\sigma_3\rangle^T$	1.30	-0.01	1.66	-0.05	1.55	-0.27	1.57	-0.71
$\langle\Delta\sigma_{11}\rangle^T$	-0.03	0.00	0.07	-0.01	0.12	-0.04	0.15	-0.17
$\langle\Delta\sigma_{12}\rangle^T$	-0.01	0.00	0.00	0.00	0.01	0.00	0.02	-0.01
$\langle\Delta\sigma_{13}\rangle^T$	0.02	0.00	0.03	0.00	0.03	0.01	0.03	0.02
$\langle\Delta\sigma_{22}\rangle^T$	0.17	0.00	-0.74	0.02	-0.98	0.10	-1.33	0.28
$\langle\Delta\sigma_{23}\rangle^T$	-0.24	0.00	-0.11	0.00	-0.07	0.19	-0.03	0.57
$\langle\Delta\sigma_{33}\rangle^T$	0.60	0.00	0.44	-0.02	0.40	-0.12	0.41	-0.40
$\langle\Delta\sigma_{44}\rangle^T$	-0.79	0.00	-0.49	0.02	-0.43	0.11	-0.35	0.28
$\langle\Delta\sigma_{45}\rangle^T$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.01
$\langle\Delta\sigma_{46}\rangle^T$	0.07	0.00	-0.01	0.00	-0.04	-0.01	-0.07	-0.03
$\langle\Delta\sigma_{55}\rangle^T$	3.51	0.01	3.06	0.01	2.94	0.03	2.70	0.10
$\langle\Delta\sigma_{56}\rangle^T$	0.04	0.00	0.03	0.00	0.02	0.00	0.02	0.01
$\langle\Delta\sigma_{66}\rangle^T$	-2.43	0.00	-3.36	-0.05	-3.76	-0.27	-4.27	-0.99
Sum	-0.01	-0.02	-1.17	-0.19	-1.94	-1.15	-2.81	-3.93

[a] In ppm. See Eq. (S1).

Table S13: Computational rovibrational contributions to the ^{1}H nuclear shielding constant, $\langle\sigma_i\rangle^T$, at $T = 300$ K for CH_3X ($X = {}^{19}$F, ^{35}Cl, ^{79}Br, ^{127}I).[a]

	CH_3F		CH_3Cl		CH_3Br		CH_3I	
	NR	BPPT	NR	BPPT	NR	BPPT	NR	BPPT
$\langle\sigma_1\rangle^T$	-0.55	0.00	-0.58	0.01	-0.66	0.02	-0.68	0.05
$\langle\sigma_2\rangle^T$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\langle\sigma_3\rangle^T$	-0.01	0.00	-0.01	0.00	-0.01	0.00	-0.02	0.00
$\langle\sigma_{11}\rangle^T$	0.01	0.00	0.02	0.00	0.02	0.01	0.03	0.02
$\langle\sigma_{12}\rangle^T$	0.00	0.00	0.00	0.00	-0.01	0.00	-0.01	0.00
$\langle\sigma_{13}\rangle^T$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\langle\sigma_{22}\rangle^T$	0.01	0.00	0.02	0.00	0.03	-0.01	0.04	-0.03
$\langle\sigma_{23}\rangle^T$	-0.02	0.00	-0.02	0.00	-0.03	0.00	-0.03	0.00
$\langle\sigma_{33}\rangle^T$	0.03	0.00	0.04	0.00	0.05	0.00	0.06	-0.03
$\langle\sigma_{4a4a}\rangle^T$	0.09	0.01	0.11	0.00	0.12	0.01	0.13	0.00
$\langle\sigma_{4a5a}\rangle^T$	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00
$\langle\sigma_{4a6a}\rangle^T$	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00
$\langle\sigma_{5a5a}\rangle^T$	-0.13	0.00	-0.11	0.00	-0.11	0.00	-0.10	0.01
$\langle\sigma_{5a6a}\rangle^T$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\langle\sigma_{6a6a}\rangle^T$	-0.11	0.00	-0.13	0.00	-0.16	0.01	-0.18	0.05
$\langle\sigma_{4b4b}\rangle^T$	0.00	0.00	0.01	0.00	0.01	0.00	0.01	-0.01
$\langle\sigma_{4b5b}\rangle^T$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\langle\sigma_{4b6b}\rangle^T$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\langle\sigma_{5b5b}\rangle^T$	-0.05	0.00	-0.05	0.00	-0.05	0.00	-0.05	0.01
$\langle\sigma_{5b6b}\rangle^T$	0.02	0.00	0.02	0.00	0.02	0.00	0.02	-0.01
$\langle\sigma_{6b6b}\rangle^T$	0.06	0.00	0.10	0.00	0.13	0.00	0.16	-0.03
Sum	-0.63	0.01	-0.58	0.01	-0.62	0.04	-0.59	0.04

[a] In ppm. See Eq. (S2).

Table S 14: Computational rovibrational contributions to the ^{1}H nuclear shielding anisotropy, $\langle\Delta\sigma_i\rangle^T$, at $T = 300$ K for CH_3X ($X = {}^{19}$F, ^{35}Cl, ^{79}Br, ^{127}I).[a]

	CH_3F		CH_3Cl		CH_3Br		CH_3I	
	NR	BPPT	NR	BPPT	NR	BPPT	NR	BPPT
$\langle\Delta\sigma_1\rangle^T$	-0.29	0.00	-0.19	0.00	-0.24	-0.01	-0.22	-0.03
$\langle\Delta\sigma_2\rangle^T$	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\langle\Delta\sigma_3\rangle^T$	-0.02	0.00	-0.04	0.00	-0.04	-0.01	-0.06	-0.01
$\langle\Delta\sigma_{11}\rangle^T$	0.08	0.00	0.05	0.00	0.07	-0.01	0.07	-0.02
$\langle\Delta\sigma_{12}\rangle^T$	0.01	0.00	0.00	0.00	0.01	0.00	0.01	0.00
$\langle\Delta\sigma_{13}\rangle^T$	-0.01	0.00	0.00	0.00	-0.01	0.00	-0.01	0.00
$\langle\Delta\sigma_{22}\rangle^T$	0.03	0.00	0.02	0.00	0.04	0.01	-0.02	0.05
$\langle\Delta\sigma_{23}\rangle^T$	0.03	0.00	0.04	0.00	0.03	0.00	0.07	-0.01
$\langle\Delta\sigma_{33}\rangle^T$	-0.05	0.00	-0.07	0.00	-0.05	0.01	-0.12	0.05
$\langle\Delta\sigma_{4a4a}\rangle^T$	0.04	0.00	0.01	0.00	0.00	0.00	-0.02	0.02
$\langle\Delta\sigma_{4a5a}\rangle^T$	-0.01	0.00	-0.01	0.00	-0.01	0.00	-0.01	0.00
$\langle\Delta\sigma_{4a6a}\rangle^T$	-0.01	0.00	-0.01	0.00	-0.02	0.00	-0.02	0.00
$\langle\Delta\sigma_{5a5a}\rangle^T$	0.03	0.00	0.01	0.00	-0.01	0.00	0.00	-0.02
$\langle\Delta\sigma_{5a6a}\rangle^T$	0.02	0.00	0.01	0.00	0.01	0.00	0.01	0.00
$\langle\Delta\sigma_{6a6a}\rangle^T$	0.11	0.00	0.23	0.00	0.30	-0.02	0.33	-0.07
$\langle\Delta\sigma_{4b4b}\rangle^T$	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	0.01
$\langle\Delta\sigma_{4b5b}\rangle^T$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\langle\Delta\sigma_{4b6b}\rangle^T$	0.00	0.00	0.00	0.00	-0.01	0.00	-0.01	0.00
$\langle\Delta\sigma_{5b5b}\rangle^T$	0.05	0.00	0.06	0.00	0.05	0.00	0.07	-0.01
$\langle\Delta\sigma_{5b6b}\rangle^T$	-0.03	0.00	-0.03	0.00	-0.03	0.00	-0.03	0.01
$\langle\Delta\sigma_{6b6b}\rangle^T$	-0.04	0.00	-0.12	0.00	-0.13	0.01	-0.20	0.05
Sum	-0.05	0.00	-0.06	0.00	-0.03	-0.01	-0.16	0.02

[a] In ppm. See Eq. (S2).

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