Supporting information on:

Tuning Halogen Bond Donor Ability: Benchmarking Substituent Effects in Fluoroiodobenzenes

Jannes N. Hasselhorn[a], Beppo Hartwig[a], Jan F. Köster[b] and Daniel A. Obenchain[a]

a Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstraße 6, 37077 Göttingen, Germany. E-mail: daniel.obenchain@uni-goettingen.de

b Institut für Organische und Biomolekulare Chemie, Georg-August-Universität Göttingen, Tammannstraße 2 37077, Göttingen, Germany.

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Additional data is made available in separate data repositories. These include raw microwave spectra, all computational outputs, and the outputs of the experimental fits.[1–3]

1 Experimental details

1.1 Synthesis of 2,3,4,5-tetrafluoroiodobenzene

2,3,4,5-tetrafluoroiodobenzene was synthesized by a modified version of a literature procedure for the similar compound 2,3,5,6-tetrafluoroiodobenzene.[4]

A 120 mL thick-walled pressure Schlenk tube (Teflon valve) was flame-dried under vacuum, allowed to cool to room temperature, charged with 2,3,4,5-tetrafluorobenzoic acid (1.00 g, 5.15 mmol, 1.0 equiv.), and evacuated (high vacuum). The vessel was transferred into a glovebox, where anhydrous K_3PO_4 (1.09 g, 5.15 mmol, 1.0 equiv.) was added. The Schlenk tube was removed from the glovebox and, under a nitrogen counter-current flow, I_2 (3.27 g, 12.88 mmol, 2.5 equiv.) was added. Anhydrous MeCN (25 mL) was then added, the tube was sealed tightly, and the reaction mixture was heated at 100 °C (oil bath) for 16 h. After cooling to room temperature, the reaction was quenched by careful addition of sat. aq. $Na_2S_2O_3$ until any visible signs of iodine disappeared, followed by addition of sat. aq. Na_2CO_3 (20 mL). The mixture was extracted with pentane (5 × 5 mL). The combined organic layers were washed with demineralized water (3 × 20 mL), dried over Na_2SO_4, filtered, and the filtrate was transferred to a Schlenk flask. Volatiles were removed under high vacuum in the following manner: The solution was frozen (liquid N_2) and subjected to dynamic high vacuum. The flask was then allowed to heat up slowly under continued evacuation until vigorous solvent outgassing/evaporation was observed. Then the sample was frozen again and the process repeated until a slowly evaporating slightly yellow liquid remained, which was immediately used for the measurement.

^{1}H NMR, ^{19}F NMR and mass spectroscopy of the slightly yellow liquid were in accordance with literature reports.[5]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (dddd, J = 9.0, 7.9, 5.2, 2.7 Hz, 1H).

^{19}F NMR (282 MHz, $CDCl_3$): δ = −117.04 (ddt, J = 22.1, 10.0, 4.5 Hz), −137.72 (dddd, J = 20.1, 11.0, 8.8, 2.8 Hz), -152.07 (ddt, J = 22.1, 19.1, 3.0 Hz), −153.70 (tdd, J = 19.6, 7.8, 4.0 Hz).

HR-MS-EI m/z calcd. for C_6HF_4I 275.0954, found 275.0964.

1.2 Synthesis of 2,3,4,6-tetrafluoroiodobenzene

2,3,4,6-tetrafluoroiodobenzene was synthesized by a modified version of a literature procedure for the similar compound 2,3,5,6-tetrafluoroiodobenzene.[4]

A 120 mL thick-walled pressure Schlenk tube (Teflon valve) was flame-dried under vacuum, allowed to cool to room temperature, charged with 2,3,4,5-tetrafluorobenzoic acid (1.00 g, 5.15 mmol, 1.0 equiv.), and evacuated (high vacuum). The vessel was transferred into a glovebox, where anhydrous K_3PO_4 (1.09 g, 5.15 mmol, 1.0 equiv.) was added. The Schlenk tube was removed from the glovebox and, under a nitrogen counter-current flow, I_2 (3.27 g, 12.88 mmol, 2.5 equiv) was added. Anhydrous MeCN (25 mL) was then added, the tube was sealed tightly, and the reaction mixture was heated at 100 °C (oil bath) for 16 h. After cooling to room temperature, the reaction was quenched by careful addition of sat. aq. $Na_2S_2O_3$ until any visible signs of iodine disappeared, followed by addition of sat. aq. Na_2CO_3 (20 mL). The mixture was extracted with pentane (5 × 5 mL). The combined organic layers were washed with demineralized water (3 × 20 mL), dried over Na_2SO_4, filtered, and the filtrate was transferred to a Schlenk flask. Volatiles were removed under high vacuum in the following manner: The solution was frozen (liquid N_2) and subjected to dynamic high vacuum. The flask was then allowed to heat up slowly under continued evacuation until vigorous solvent outgassing/evaporation was observed. Then the sample was frozen again and the process repeated until only a slowly evaporating slightly pink liquid remained, which was immediately used for the measurement.

^{1}H NMR, ^{19}F NMR and mass spectroscopy of the slightly yellow liquid were in accordance with literature reports.[6]

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.88$ (dddd, $J = 10.0$, 7.5, 5.9 2.5 Hz, 1H).

^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -96.21$ (ddt, $J = 9.6$, 7.1, 2.2 Hz), -111.64 (ddt, $J = 22.8$, 6.8, 2.0 Hz), -131.01 (dddd, $J = 20.0$, 9.8, 6.5, 2.8 Hz), -161.75 (dddd, $J = 22.1$, 20.6, 9.8, 5.9 Hz).

HR-MS-EI m/z calcd. for C_6HF_4I 275.0954, found 275.0958.

1.3 List of Chemicals

The chemicals listed in Tab. S1 were used without further purification. In the case of 2,3,5-trifluoroiodobenzene, no information regarding purity was provided by the manufacturer. No rotational spectroscopy active impurities were detected.

Tab. S1: Overview of the chemicals used with their respective CAS-number, manufacturer and purity.

Substance	CAS-number	Manufacturer	Purity
2-fluoroiodobenzene	348-52-7	BLDpharm	99.81%
3-fluoroiodobenzene	1121-86-4	BLDpharm	99.86%
4-fluoroiodobenzene	352-34-1	BLDpharm	99.29%
2,3-difluoroiodobenzene	64248-57-3	Chemat	98%
2,4-difluoroiodobenzene	2265-93-2	AmBeed	99.83%
2,5-difluoroiodobenzene	2265-92-1	AmBeed	99.48%
2,6-difluoroiodobenzene	13697-89-7	BLDpharm	98%
3,4-difluoroiodobenzene	64248-58-4	Fluorochem	99%
3,5-difluoroiodobenzene	2265-91-0	AmBeed	98%
2,3,4-trifluoroiodobenzene	459424-72-7	AmBeed	99.19%
2,3,5-trifluoroiodobenzene	622379-51-5	abcr	—
2,3,6-trifluoroiodobenzene	1190385-24-0	abcr	95%
2,4,6-trifluoroiodobenzene	41860-63-3	AOBChem	97%
3,4,5-trifluoroiodobenzene	170112-66-0	BLDpharm	98%
2,3,5,6-tetrafluoroiodobenzene	5243-24-3	abcr	97%
pentafluoroiodobenzene	827-15-6	BLDpharm	98%

1.4 Fits

Tab. S2: A comparison of the experimental results for iodobenzene, taken from Ref. [7], and theory. The data supplied in the supplementary information has been refitted in order to convert the Watson A to Watson S reduction in the I^r representation. The rotational constants A, B and C are compared to the scaled parameters, as described in Sec. 2.3 of the main text. The distortion constants D_J, D_{JK}, D_K, d_1, d_2, H_{JK} and H_{KJ} are compared to a VPT2 calculation at the B3LYP-D3(BJ)/def2-TZVP level of theory. Results for the nuclear quadrupole coupling constants, χ_{aa}, χ_{bb}, χ_{cc} and $|\chi_{ab}|$, of the inertial principal axis system are compared with the results obtained from a parametrisation based on the same training set employing calculations at Bailey's B1LYP/6-311G(df,p) level of theory. For iodine, a f-polarization function with a coefficient of 0.4 was added to the 6-311G(d,p) basis set. The linearly dependent uncertainties of the χ_{ii} were calculated from the uncertainty in Q_{eff}, which may result in an underestimation of the actual uncertainties. Additionally, the asymmetry of the nuclear quadrupole coupling tensor η was calculated in the nuclear principal axis system. The corresponding NQCCs are shown in Tab. S22. The spin-rotation constants C_{aa}, C_{bb} and C_{cc} have not been calculated. Given the $C_{2\text{v}}$ symmetry of the system, the total dipole moment μ_{total} is equal to the component in the a-direction. Additionally, the total number of fitted transitions N_{total} as well as the number of unique transition neglecting hyperfine splitting (N_{NHS}) are given.

	Experiment [7]	Theory
A / MHz	5669.128(15)	5709.367
B / MHz	750.414 014(53)	750.214
C / MHz	662.636 470(44)	662.714
D_J / kHz	0.018 862 3(11)	0.0184
D_{JK} / kHz	0.168 740(67)	0.158
D_K / kHz	0.883(52)	1.010
d_1 / kHz	−0.002 530 98(65)	0.002 44
d_2 / kHz	−0.000 342 78(72)	−0.000 318
H_{JK} / Hz	0.000 054 1(13)	0.000 004 52
H_{KJ} / Hz	−0.000 356(16)	−0.000 374
χ_{aa} / MHz	−1892.0398(46)	−1896(7)
χ_{bb} / MHz	978.821(12)	1002(4)
χ_{cc} / MHz	913.219(12)	894(3)
η	0.034 673(9)	0.0572(24)
C_{aa} / MHz	0.001 66(86)	—
C_{bb} / MHz	0.002 60(13)	—
C_{cc} / MHz	0.002 60(13)	—
$\mu_{\text{total}} = \mu_a$ / D	1.6250(20)	1.68
$N_{\text{total}}(N_{\text{NHS}})$	310(290)	—
σ / kHz	3.50	—

Tab. S3: A comparison between the experimental results (Watson S reduction in I^r representation) and the theoretical results for 2-fluoroiodobenzene, 3-fluoroiodobenzene, and 4-fluoroiodobenzene. The rotational constants A, B and C are compared to the scaled parameters, as described in Sec. 2.3 of the main text. The distortion constants D_J, D_{JK}, D_K, d_1, d_2 are compared to a VPT2 calculation at the B3LYP-D3(BJ)/def2-TZVP level of theory. Results for the nuclear quadrupole coupling constants, χ_{aa}, χ_{bb}, χ_{cc} and $|\chi_{ab}|$, of the inertial principal axis system are compared with the results obtained from a parametrisation based on the same training set employing calculations at Bailey's B1LYP/6-311G(df,p) level of theory. For iodine, a f-polarization function with a coefficient of 0.4 was added to the 6-311G(d,p) basis set. The linearly dependent uncertainties of the χ_{ii} were calculated from the uncertainty in Q_{eff}, which may result in an underestimation of the actual uncertainties. Additionally, the asymmetry of the nuclear quadrupole coupling tensor η was calculated in the nuclear principal axis system. The corresponding NQCCs are shown in Tab. S22. No comparison to theory is drawn for the spin-rotation constants C_{aa}, C_{bb} and C_{cc}. Only the non-zero dipole components μ_a and μ_b are provided. For 4-fluoroiodobenzene, μ_a equals the total dipole moment due to $C_{2\mathrm{v}}$ symmetry. Additionally, the total number of fitted transitions N_{total} as well as the number of unique transition neglecting hyperfine splitting (N_{NHS}) are given.

	2-fluoroiodobenzene		3-fluoroiodobenzene		4-fluoroiodobenzene	
	Experiment	Theory	Experiment	Theory	Experiment	Theory
A / MHz	2826.233 41(28)	2825.665	3260.244 58(13)	3265.615	5643.216(34)	
B / MHZ	735.182 199(76)	734.930	560.829 864(49)	560.896	474.978 79(10)	
C / MHz	583.340 14(10)	583.239	478.463 434(48)	478.503	438.107 853(92)	
D_J / kHz	0.008 86(93)	0.0158	0.010 12(13)	0.009 71	0.006 26(16)	0.006 12
D_{JK} / kHz	0.2007(29)	0.205	0.0345(14)	0.303	—	0.0307
D_K / kHz	—	0.277	0.7281(87)	0.739	—	1.105 902
d_1 / kHz	—	−0.003 49	−0.002 380(44)	−0.001 84	—	0.000 537
d_2 / kHz	−0.003 06(11)	−0.001 03	—	−0.000 243	—	−0.000 041
χ_{aa} / MHz	−2010.6979(54)	−2012(7)	−1828.3649(31)	−1830(6)	−1922.85(11)	−1930(7)
χ_{bb} / MHz	1067.4761(75)	1092(4)	901.2932(34)	924(3)	987.60(11)	1011(4)
χ_{cc} / MHz	943.2217(75)	920(3)	927.0716(34)	905(3)	935.25(11)	919(3)
$\|\chi_{ab}\|$ / MHz	117.074(31)	107(1)	533.8905(70)	537(20)	0	
η / MHz	0.063 867(5)	0.0873(24)	0.038 842(3)	0.0624(22)	0.027 224(85)	0.0479(24)
C_{aa} / MHz	—	—	—	—	—	—
C_{bb} / MHz	0.002 270(96)	—	0.001 780(70)	—	—	—
C_{cc} / MHz	0.001 65(10)	—	0.001 761(64)	—	0.001 91(44)	—
μ_a / D	strong	1.90	weak	0.47	very weak	0.06
μ_b / D	medium	1.28	medium	1.43	not observed	0
$N_{\mathrm{total}}(N_{\mathrm{NHS}})$	119(24)	—	247(49)	—	46(14)	—
σ / kHz	2.69	—	2.53	—	1.96	—

Tab. S4: A comparison between the experimental results (Watson S reduction in I^r representation) and the theoretical results for the difluoroiodobenzenes. The rotational constants A, B and C are compared to the scaled parameters, as described in Sec. 2.3 of the main text. The distortion constants D_J, D_{JK}, D_K, d_1, d_2 are compared to a VPT2 calculation at the B3LYP-D3(BJ)/def2-TZVP level of theory. Results for the nuclear quadrupole coupling constants, χ_{aa}, χ_{bb}, χ_{cc} and $|\chi_{ab}|$, of the inertial principal axis system are compared with the results obtained from a parametrisation based on the same training set employing calculations at Bailey's B1LYP/6-311G(df,p) level of theory. For iodine, a f-polarization function with a coefficient of 0.4 was added to the 6-311G(d,p) basis set. The linearly dependent uncertainties of the χ_{ii} were calculated from the uncertainty in Q_{eff}, which may result in an underestimation of the actual uncertainties. Additionally, the asymmetry of the nuclear quadrupole coupling tensor η was calculated in the nuclear principal axis system. The corresponding NQCCs are shown in Tab. S22. No comparison to theory is drawn for the spin-rotation constants C_{aa}, C_{bb} and C_{cc}. Only the non-zero dipole components μ_a and μ_b are provided. For 2,6-difluoroiodobenzene and 3,5-difluoroiodobenzene, μ_a equals the total dipole moment due to C_{2v} symmetry. Additionally, the total number of fitted transitions N_{total} as well as the number of unique transition neglecting hyperfine splitting (N_{NHS}) are given.

	2,3-difluoroiodobenzene		2,4-difluoroiodobenzene		2,5-difluoroiodobenzene	
	Experiment	Theory	Experiment	Theory	Experiment	Theory
A / MHz	2254.841 62(12)	2256.805	2788.202 14(65)	2787.396	1895.973 30(81)	1888.769
B / MHZ	551.937 243(48)	551.614	472.708 18(19)	472.583	558.490 85(10)	558.965
C / MHz	443.370 257(53)	443.244	404.169 05(18)	403.922	431.355 688(56)	431.382
D_J / kHz	0.001 42(28)	0.009 39	0.019 78(91)	0.005 41	0.008 28(12)	0.007 94
D_{JK} / kHz	0.064 47(65)	0.0585	0.0863(15)	0.0703	0.0417(16)	0.0443
D_K / kHz	0.0777(33)	0.0716	−0.403(62)	0.556	−0.109(14)	0.356
d_1 / kHz	−0.002 513(67)	−0.002 19	—	−0.000 802	−0.002 35(12)	−0.002 27
d_2 / kHz	−0.000 345(36)	−0.000 418	0.000 182(26)	−0.000 154	−0.000 468(51)	−0.000 498
χ_{aa} / MHz	−1909.7101(39)	−1914(7)	−2041.8488(53)	−2045(7)	−1918.282(11)	−1912(7)
χ_{bb} / MHz	952.9745(39)	981(4)	1076.5010(51)	1100(4)	963.134(20)	983(4)
χ_{cc} / MHz	956.7357(39)	932(3)	965.3478(51)	945(4)	955.148(20)	929(3)
$\|\chi_{ab}\|$ / MHz	637.4949(66)	627(2)	9.583(56)	21(1)	625.3912(85)	639(3)
η	0.064 435(3)	0.0877(22)	0.054 451(4)	0.0755(24)	0.067 312(9)	0.0920(22)
C_{aa} / MHz	—	—	0.001 15(10)	—	—	—
C_{bb} / MHz	0.001 599(73)	—	0.001 981(88)	—	0.001 69(19)	—
C_{cc} / MHz	0.001 171(75)	—	—	—	0.001 13(14)	—
μ_a / D	medium	0.47	not observed	0.36	medium	0.98
μ_b / D	very strong	2.57	medium	1.17	very weak	0.34
$N_{\mathrm{total}}(N_{\mathrm{NHS}})$	179(54)	—	127(21)	—	83(20)	—
σ / kHz	2.63	—	2.19	—	1.36	—

S4 continued.

	2,6-difluoroiodobenzene		3,4-difluoroiodobenzene		3,5-difluoroiodobenzene	
	Experiment	Theory	Experiment	Theory	Experiment	Theory
A / MHz	1749.423 83(83)	1746.056	3023.506 77(26)	3025.513	1760.365 35(18)	1758.332
B / MHZ	725.773 667(43)	725.736	406.990 805(39)	407.043	482.492 572(56)	482.625
C / MHz	512.905 760(31)	512.938	358.692 155(23)	358.580	378.650 201(27)	378.708
D_J / kHz	—	0.0119	0.004 105(80)	0.004 07	0.005 162(77)	0.005 13
D_{JK} / kHz	0.1523(18)	−0.0547	0.0305(20)	0.0303	0.057 90(53)	0.0556
D_K / kHz	0.860(73)	0.142	0.562(29)	0.507	—	0.0442
d_1 / kHz	—	0.004 46	−0.000 544(38)	−0.000 572	−0.001 344(65)	0.001 39
d_2 / kHz	—	−0.001 93	—	−0.000 075	−0.000 398(33)	−0.000 396
χ_{aa} / MHz	−2134.8446(54)	−2133(7)	−1915.804(57)	−1918(7)	−1967.122(11)	−1968(7)
χ_{bb} / MHz	1163.1885(47)	1187(4)	968.408(29)	991(4)	1025.969(11)	1050(4)
χ_{cc} / MHz	971.6561(47)	945(4)	947.396(29)	927(3)	941.153(11)	918(3)
$\lvert\chi_{ab}\rvert$ / MHz	0	0	340.011(12)	342(2)	0	0
η	0.089 717 3(31)	0.1136(24)	0.030 968(21)	0.0526(23)	0.043 116 8(78)	0.0672(24)
C_{aa} / MHz	—	—	—	—	—	—
C_{bb} / MHz	—	—	0.001 390(80)	—	0.001 46(16)	—
C_{cc} / MHz	0.001 83(13)	—	0.001 285(67)	—	0.001 52(11)	—
μ_a / D	very strong	2.27	weak	0.91	weak	0.21
μ_b / D	not observed	0	medium	1.17	not observed	0
$N_{\text{total}}(N_{\text{NHS}})$	171(31)	—	77(21)	—	236(58)	—
σ / kHz	2.93	—	1.31	—	2.15	—

Tab. S5: A comparison between the experimental results (Watson S reduction in I^r representation) and the theoretical results for the trifluoroiodobenzenes. The rotational constants A, B and C are compared to the scaled parameters, as described in Sec. 2.3 of the main text. The distortion constants D_J, D_{JK}, D_K, d_1, d_2 are compared to a VPT2 calculation at the B3LYP-D3(BJ)/def2-TZVP level of theory. Results for the nuclear quadrupole coupling constants, χ_{aa}, χ_{bb}, χ_{cc} and $|\chi_{ab}|$, of the inertial principal axis system are compared with the results obtained from a parametrisation based on the same training set employing calculations at Bailey's B1LYP/6-311G(df,p) level of theory. For iodine, a f-polarization function with a coefficient of 0.4 was added to the 6-311G(d,p) basis set. The linearly dependent uncertainties of the χ_{ii} were calculated from the uncertainty in Q_{eff}, which may result in an underestimation of the actual uncertainties. Additionally, the asymmetry of the nuclear quadrupole coupling tensor η was calculated in the nuclear principal axis system. The corresponding NQCCs are shown in Tab. S22. No comparison to theory is drawn for the spin-rotation constants C_{aa}, C_{bb} and C_{cc}. Only the non-zero dipole components μ_a and μ_b are provided. For 246-trifluoroiodobenzene and 345-trifluoroiodobenzene, μ_a equals the total dipole moment due to C_{2v} symmetry. Additionally, the total number of fitted transitions N_{total} as well as the number of unique transition neglecting hyperfine splitting (N_{NHS}) are given.

	2,3,4-trifluoroiodobenzene		2,3,5-trifluoroiodobenzene		2,3,6-trifluoroiodobenzene	
	Experiment	Theory	Experiment	Theory	Experiment	Theory
A / MHz	2062.262 76(12)	2061.273	1324.396 08(18)	1321.308	1441.8107(30)	1438.738
B / MHZ	405.827 205(70)	405.769	481.222 520(88)	481.342	549.387 257(98)	549.528
C / MHz	339.090 607(49)	338.943	352.938 405(40)	352.951	397.783 298(42)	397.823
D_J / kHz	0.005 19(20)	0.003 82	0.004 26(18)	0.004 51	0.007 492(75)	0.007 56
D_{JK} / kHz	0.043 12(76)	0.0403	0.0498(20)	0.0494	−0.5373(18)	0.0348
D_K / kHz	0.1242(48)	0.123	0.0157(34)	0.005 74	−2.199(42)	0.0674
d_1 / kHz	−0.000 347(30)	−0.000 677	−0.001 25(11)	−0.001 53	—	−0.002 69
d_2 / kHz	—	−0.000 134	−0.000 441(44)	−0.000 560	—	−0.000 673
χ_{aa} / MHz	−2030.3252(43)	−2032(12)	−2080.709(27)	−2078(7)	−1968.000(87)	−1964(7)
χ_{bb} / MHz	1052.3516(47)	1076(6)	1111.113(16)	1134(4)	983.658(65)	1008(4)
χ_{cc} / MHz	977.9736(47)	956(6)	969.596(16)	943(4)	984.342(65)	956(4)
$\|\chi_{ab}\|$ / MHz	345.356(11)	332(1)	19.00(20)	32(1)	779.299(45)	780(3)
η	0.054 432(3)	0.0751(23)	0.068 065(11)	0.0920(24)	0.089 043(42)	0.1128(22)
C_{aa} / MHz	—	—	—	—	—	—
C_{bb} / MHz	0.001 329(68)	—	0.001 96(26)	—	—	—
C_{cc} / MHz	0.000 971(85)	—	—	—	0.001 00(13)	—
μ_a / D	weak	0.75	not observed	0.09	medium	1.00
μ_b / D	strong	2.27	weak	1.08	weak	1.51
$N_{\text{total}}(N_{\text{NHS}})$	127(35)	—	118(34)	—	136(34)	—
σ / kHz	2.00	—	2.31	—	2.32	—

S5 continued.

	2,4,5-trifluoroiodobenzene		2,4,6-trifluoroiodobenzene		3,4,5-trifluoroiodobenzene	
	Experiment	Theory	Experiment	Theory	Experiment	Theory
A / MHz	1840.621 53(66)	1834.028	1748.4661(42)	1745.618	1757.5626(83)	1755.038
B / MHZ	405.739 055(44)	406.016	471.013 17(12)	470.987	369.544 921(76)	369.696
C / MHz	332.438 944(32)	332.374	371.048 711(72)	370.927	305.327 276(74)	305.310
D_J / kHz	0.003 591(32)	0.003 44	0.004 11(26)	0.004 54	0.002 48(15)	0.002 71
D_{JK} / kHz	0.029 24(37)	0.0281	0.0503(14)	0.0486	0.0235(21)	0.0304
D_K / kHz	0.221(29)	0.258	—	0.0450	—	0.0751
d_1 / kHz	−0.000 754(31)	−0.000 740	−0.000 60(16)	0.001 10	—	0.000 562
d_2 / kHz	−0.000 161(16)	−0.000 149	—	−0.000 299	—	−0.000 129
χ_{aa} / MHz	−2009.819(16)	−2005(7)	−2159.943(16)	−2160(8)	−1991.46(17)	−1991(7)
χ_{bb} / MHz	1033.452(14)	1052(4)	1165.962(14)	1189(4)	1030.56(11)	1052(4)
χ_{cc} / MHz	976.367(14)	953(4)	993.982(14)	970(4)	960.90(11)	939(4)
$\|\chi_{ab}\|$ / MHz	441.5790(70)	455(2)	0	0	0	0
η	0.057 833(10)	0.0801(23)	0.079 622(9)	0.1011(24)	0.034 983(80)	0.0571(24)
C_{aa} / MHz	—	—	—	—	—	—
C_{bb} / MHz	0.000 92(14)	—	—	—	—	—
C_{cc} / MHz	0.000 85(12)	—	—	—	—	—
μ_a / D	weak	0.46	medium	0.69	weak	1.61
μ_b / D	weak	0.05	not observed	0	not observed	0
$N_{\mathrm{total}}(N_{\mathrm{NHS}})$	244(58)	—	80(16)	—	52(16)	—
σ / kHz	2.21	—	2.36	—	2.77	—

Tab. S6: A comparison between the experimental results (Watson S reduction in I^r representation) and the theoretical results for the tetrafluoroiodobenzenes. The rotational constants A, B and C are compared to the scaled parameters, as described in Sec. 2.3 of the main text. The distortion constants D_J, D_{JK}, D_K, d_1, d_2 are compared to a VPT2 calculation at the B3LYP-D3(BJ)/def2-TZVP level of theory. Results for the nuclear quadrupole coupling constants, χ_{aa}, χ_{bb}, χ_{cc} and $|\chi_{ab}|$, of the inertial principal axis system are compared with the results obtained from a parametrisation based on the same training set employing calculations at Bailey's B1LYP/6-311G(df,p) level of theory. For iodine, a f-polarization function with a coefficient of 0.4 was added to the 6-311G(d,p) basis set. The linearly dependent uncertainties of the χ_{ii} were calculated from the uncertainty in Q_{eff}, which may result in an underestimation of the actual uncertainties. Additionally, the asymmetry of the nuclear quadrupole coupling tensor η was calculated in the nuclear principal axis system. The corresponding NQCCs are shown in Tab. S22. No comparison to theory is drawn for the spin-rotation constants C_{aa}, C_{bb} and C_{cc}. Only the non-zero dipole components μ_a and μ_b are provided. For 2356-tetrafluoroiodobenzene, μ_a equals the total dipole moment due to C_{2v} symmetry. Additionally, the total number of fitted transitions N_{total} as well as the number of unique transition neglecting hyperfine splitting (N_{NHS}) are given.

	2,3,4,5-tetrafluoroiodobenzene		2,3,4,6-tetrafluoroiodobenzene		2,3,5,6-tetrafluoroiodobenzene	
	Experiment	Theory	Experiment	Theory	Experiment	Theory
A / MHz	1320.744 560(43)	1317.344	1377.787 479(67)	1374.670	1027.611 04(42)	1025.382
B / MHz	369.063 239(20)	369.256	404.619 743(18)	404.774	480.273 85(12)	480.397
C / MHz	288.448 430(14)	288.437	312.765 579(15)	312.742	327.284 494(28)	327.366
D_J / kHz	0.002 493(33)	0.002 41	0.003 228(34)	0.003 15	0.003 70(12)	0.003 79
D_{JK} / kHz	0.028 17(13)	0.0267	0.026 98(21)	0.0251	0.044 62(44)	0.0406
D_K / kHz	0.043 61(82)	0.0359	0.0381(17)	0.0376	0.0145(35)	−0.0228
d_1 / kHz	−0.000 656(15)	−0.000 626	−0.000 886(13)	−0.000 866	−0.001 53(10)	0.001 69
d_2 / kHz	−0.000 196 4(88)	−0.000 182	−0.000 223 5(45)	−0.000 220	−0.000 539(38)	−0.000 752
χ_{aa} / MHz	−2101.8329(31)	−2098(7)	−2119.1043(39)	−2116(7)	−2192.339(38)	−2186(8)
χ_{bb} / MHz	1111.2775(32)	1131(4)	1112.9900(30)	1135(4)	1194.012(32)	1216(4)
χ_{cc} / MHz	990.5555(32)	966(4)	1006.1144(30)	981(4)	998.328(32)	970(4)
$\|\chi_{ab}\|$ / MHz	72.676(14)	88(1)	466.8451(33)	465(2)	0	0
η	0.058 173(2)	0.0796(24)	0.079 149(2)	0.1003(23)	0.089 258(21)	0.1123(24)
C_{aa} / MHz	—	—	0.000 867(86)	—	—	—
C_{bb} / MHz	0.001 193(55)	—	0.001 187(51)	—	—	—
C_{cc} / MHz	0.000 907(56)	—	0.000 671(49)	—	0.000 98(13)	—
μ_a / D	medium	1.28	weak	0.30	very weak	0.42
μ_b / D	medium	1.08	strong	1.16	not observed	0
$N_{\text{total}}(N_{\text{NHS}})$	439(94)	—	470(110)	—	177(44)	—
σ / kHz	1.82	—	2.09	—	2.34	—

Tab. S7: A comparison between the experimental results (Watson S reduction in I^r representation) and the theoretical results for pentafluoroiodobenzene. The rotational constants A, B and C are compared to the scaled parameters, as described in Sec. 2.3 of the main text. The distortion constants D_J, D_{JK}, D_K, d_1, d_2 are compared to a VPT2 calculation at the B3LYP-D3(BJ)/def2-TZVP level of theory. Results for the nuclear quadrupole coupling constants, χ_{aa}, χ_{bb}, χ_{cc} and $|\chi_{ab}|$, of the inertial principal axis system are compared with the results obtained from a parametrisation based on the same training set employing calculations at Bailey's B1LYP/6-311G(df,p) level of theory. For iodine, a f-polarization function with a coefficient of 0.4 was added to the 6-311G(d,p) basis set. The linearly dependent uncertainties of the χ_{ii} were calculated from the uncertainty in Q_{eff}, which may result in an underestimation of the actual uncertainties. Additionally, the asymmetry of the nuclear quadrupole coupling tensor η was calculated in the nuclear principal axis system. The corresponding NQCCs are shown in Tab. S22. No comparison to theory is drawn for the spin-rotation constants C_{aa}, C_{bb} and C_{cc}. Given the $C_{2\text{v}}$ symmetry of the system, the total dipole moment μ_{total} is equal to the component in the a-direction. Additionally, the total number of fitted transitions N_{total} as well as the number of unique transition neglecting hyperfine splitting (N_{NHS}) are given.

	Experiment	Theory
A / MHz	1027.236 28(12)	1024.916
B / MHz	368.813 333(45)	369.016
C / MHz	271.378 409(26)	271.427
D_J / kHz	0.002 044(40)	0.002 10
D_{JK} / kHz	0.022 73(26)	0.0215
D_K / kHz	—	−0.001 76
d_1 / kHz	0.000 672(41)	0.000 702
d_2 / kHz	0.000 225(14)	−0.000 245
χ_{aa} / MHz	−2216.522(10)	−2210(8)
χ_{bb} / MHz	1196.244(13)	1216(4)
χ_{cc} / MHz	1020.278(13)	994(4)
η	0.079 389(8)	0.1001(24)
C_{aa} / MHz	0.001 192(90)	—
C_{bb} / MHz	—	—
C_{cc} / MHz	—	—
$\mu_{\text{total}} = \mu_a$ / D	0.97	medium
$N_{\text{total}}(N_{\text{NHS}})$	294(68)	—
σ / kHz	1.62	—

Tab. S8: Experimentally determined planar moments P_{aa}, P_{bb}, and P_{cc}. The nomenclature of the molecules in the left-hand column is explained in Fig. 1 of the main text.

Molecule	P_{aa} / amu Å^2	P_{bb} / amu Å^2	P_{cc} / amu Å^2
0	673.500 12(12)	89.179 02(12)	−0.033 21(12)
2	687.478 419(83)	178.875 487(83)	−0.058 335(83)
3	901.184 362(57)	155.069 832(57)	−0.057 226(57)
4	1063.998 74(32)	89.550 56(32)	0.004 58(32)
23	915.686 449(79)	224.171 268(79)	−0.040 666(79)
24	1069.136 42(35)	181.278 49(35)	−0.022 26(35)
25	904.976 75(12)	266.629 47(12)	−0.075 61(12)
26	696.386 791(78)	288.938 488(78)	−0.055 366(78)
34	1241.772 363(75)	167.176 793(75)	−0.026 842(75)
35	1047.515 946(79)	287.169 755(79)	−0.082 186(79)
234	1245.320 32(15)	245.074 87(15)	−0.014 43(15)
235	1050.262 28(13)	381.656 16(13)	−0.064 11(13)
236	919.933 56(38)	350.554 70(38)	−0.037 80(38)
245	1245.611 35(11)	274.604 67(11)	−0.034 91(11)
246	1072.974 46(40)	289.054 29(40)	−0.012 93(40)
345	1367.615 07(72)	287.589 20(72)	−0.043 82(72)
2345	1369.384 632(57)	382.675 551(57)	−0.028 501(57)
2346	1249.028 480(49)	366.811 123(49)	−0.006 360(49)
2356	1052.315 41(18)	491.842 72(18)	−0.042 81(18)
23456	1370.285 75(13)	491.981 08(13)	−0.001 75(13)

Tab. S9: Rotation angles α_{az} between the inertial principal axis a and the nuclear principal axis z. Only the fluorinated iodobenzenes of C_s symmetry are shown. The nomenclature of the molecules in the left-hand column is explained in Fig. 1 of the main text.

Molecule	α_{az} / °
2	2.1750(6)
3	10.6822(1)
23	12.0037(1)
24	0.1761(10)
25	11.7325(2)
34	6.6333(3)
234	6.3146(2)
235	0.3410(40)
236	13.9180(8)
245	8.0914(1)
2345	1.2951(2)
2346	8.0565(1)

1.5 Spectral Directory

Tab. S10: Overview of the experimental conditions for all scans used for fitting during this work. Start and end frequencies, ν_{start} and ν_{end}, number of averages, carrier gas, stagnation pressures p_s and sample temperatures T_s are given. Individual single measurements are not shown. Given the non-existence of conformational space for these systems, the carrier gases were changed between measurements to avoid interference with other projects. More details can be found at `https://data.goettingen-research-online.de/privateurl.xhtml?token=04d42688-d4a9-4788-be47-708431c9fc4c`.

Substance	Experiment	ν_{start} / MHz	ν_{end} / MHz	Averages	Gas	p_s / bar	T_s / K
2-fluoroiodobenzene	7800p	7800.0	7910.0	350	He	1.24	298
	7900p	7900.0	8473.5	350	He	1.24	298
	8400p	8400.0	8677.5	350	He	1.24	298
3-fluoroiodobenzene	8080p	8080.0	8110.6	350	He	1.24	298
	8080p_opt	8080.0	8254.0	350	He	1.24	298
	8244	8080.0	8427.6	350	He	1.24	298
	8414_changed_settings	8414.0	8801.9	350	He	1.24	298
	13540p	13 540.0	13 776.7	350	He	1.24	298
4-fluoroiodobenzene	8036p	8036.4	7910.0	7500	Ne	1.50	358
	9090p	9090.0	9162.79	2000	Ne	1.50	358
2,3-difluoroiodobenzene	7900p	7900.0	7935.1	350	Ne	1.24	298
	7900popt	7900.0	7964.2	350	Ne	1.24	298
	7960pnewsettings	7960.0	8011.9	350	Ne	1.24	298
	8000pnewmode	8000.0	8361.5	350	Ne	1.24	298
	15600p	15 600.0	15 699.0	350	Ne	1.24	298
2,4-difluoroiodobenzene	8220p	8220.0	8385.3	350	Ne	1.24	298
	11550p	11 550.0	11 976.3	350	Ne	1.24	298
2,5-difluoroiodobenzene	7810p	7810.0	7832.2	350	Ne	1.24	298
	7810p_opt	7810.0	7873.3	350	Ne	1.24	298
	7871p	7971.0	8049.5	350	Ne	1.24	298
	12505p	12 505.0	12 558.7	350	Ne	1.24	298
	15069p	15 069.0	15 170.7	350	Ne	1.24	298
2,6-difluoroiodobenzene	7500p	7500.0	8151.0	350	He	1.24	298
	8140p	8140.0	8455.9	350	He	1.24	298
	8443p	8443.5	8472.1	350	He	1.24	298
	8466p	8466.5	8952.5	350	He	1.24	298
	8938p	8938.0	9082.0	350	He	1.24	298

	8390p	8390.0	8390.6	350	Ne	1.24	298
	8390p_opt	8390.0	8585.6	350	Ne	1.24	298
3,4-difluoroiodobenzene	10208p	10 208.0	10 261.1	350	Ne	1.24	298
	15091p	15 091.0	15 131.2	350	Ne	1.24	298
	15730p	15 730.0	15 769.9	350	Ne	1.24	298
	7979p	7979.0	7987.4	350	Ne	1.10	298
	7979pv2	7979.0	7998.5	300	Ne	1.10	298
	8452p	8452.0	8549.2	400	Ne	1.10	298
	8662p	8662.0	8768.2	350	Ne	1.10	298
3,5-difluoroiodobenzene	9448p	9448.0	9655.0	400	Ne	1.10	298
	10360p	10 360.0	10 490.2	450	Ne	1.10	298
	11732p	11 732.0	11 752.7	400	Ne	1.10	298
	13957p	13 957.0	14 018.8	450	Ne	1.10	298
	14752p	14 752.0	14 780.8	400	Ne	1.10	298
	15516p	15 516.0	15 517.2	300	Ne	1.10	298
	8050p	8050.0	8074.6	350	Ne	1.24	298
2,3,4-trifluoroiodobenzene	8050p_opt	8050.0	8293.9	350	Ne	1.24	298
	15100p	15 100.0	15 108.4	350	Ne	1.24	298
	7908p	7908.0	7913.4	350	Ar	1.10	298
	7910p	7910.0	7910.6	350	Ar	1.10	298
	8490p	8490.0	8491.5	350	Ar	1.10	298
	8810p	8881.0	8864.0	350	Ar	1.10	298
	9520p	9520.0	9520.3	350	Ar	1.10	298
2,3,5-trifluoroiodobenzene	10832p	10 830.0	10 873.2	350	Ar	1.10	298
	11644p	11 644.0	11 704.9	350	Ar	1.10	298
	12350p	12 350.0	12 367.4	350	Ar	1.10	298
	13048p	13 048.0	13 108.0	350	Ar	1.10	298
	13760p	13 760.0	13 844.3	350	Ar	1.10	298
	13760p_cont	13 844.6	14 066.3	350	Ar	1.10	298
	14471p	14 471.0	14 481.2	350	Ar	1.10	298
	8320p	8320.0	8392.9	350	Ar	1.10	298
	9112p	9112.0	9192.1	350	Ar	1.10	298
	9936p	9936.0	9949.8	350	Ar	1.10	298
2,3,6-trifluoroiodobenzene	11521p	11 521.0	11 590.0	350	Ar	1.10	298
	12326p	12 326.0	12 338.3	350	Ar	1.10	298
	13126p	13 126.0	13 135.0	350	Ar	1.10	298
	14716p	14 716.0	14 721.4	350	Ar	1.10	298

2,4,5-trifluoroiodobenzene	8147p	8147.0	8170.7	200	Ne	1.24	298
	9000p	9000.0	9049.8	200	Ne	1.24	298
	9620p	9620.0	9687.2	200	Ne	1.24	298
	10290p	10 290.0	10 540.5	350	Ne	1.24	298
	11093p	11 093.0	11 156.6	300	Ne	1.24	298
	12218p	12 218.0	12 231.8	200	Ne	1.24	298
	12294p	12 294.0	12 309.9	300	Ne	1.24	298
	13626p8p	13 626.8	13 644.8	400	Ne	1.24	298
	15433p	15 433.0	15 449.5	300	Ne	1.24	298
	15433pv2	15 433.0	15 449.2	250	Ne	1.24	298
	15433pv3	15 433.0	15 442.0	4000	Ne	1.24	298
2,4,6-trifluoroiodobenzene	7500p	7500.0	7559.7	350	He	1.24	298
	7535p	7535.0	8083.1	350	He	1.24	298
	7708p	7708.4	7731.4	350	He	1.24	298
	14468p	14 468.9	14 480.7	350	He	1.24	298
3,4,5-trifluoroiodobenzene	7500p	7500.0	8150.8	150	He	1.24	298
	7900p	7900.0	8367.0	150	He	1.24	298
2,3,4,5-tetrafluoroiodobenzene	7196p	7196.0	7565.0	200	Ne	1.60	298
	9217p	9217.0	9331.9	250	Ne	1.60	298
	9839p	9839.0	10 273.4	250	Ne	1.60	298
	10655p	10 655.0	10 837.7	250	Ne	1.60	298
	10838p	10 838.0	10 876.1	250	Ne	1.60	298
	11817p	11 816.0	11 830.1	200	Ne	1.60	298
2,3,4,6-tetrafluoroiodobenzene	7760p	7760.0	8021.9	500	Ne	1.60	298
	8416p	8416.0	9253.3	350	Ne	1.60	298
	10313p	10 313.0	10 330.7	300	Ne	1.60	298
	12075p	12 075.0	12 671.4	300	Ne	1.60	298
	12830p	12 830.0	12 833.9	300	Ne	1.60	298
	15556p	15 556.0	15 637.0	350	Ne	1.60	298
2,3,5,6-tetrafluoroiodobenzene	8170p	8170.0	8357.5	500	He	1.24	338
	8835p	8835.0	8847.3	200	He	1.24	338
	9480p	9480.0	9482.7	400	He	1.24	338
	9480_cont	9483.0	9513.3	400	He	1.24	338
	10142p	10 142.0	10 158.8	500	He	1.24	338
	11453p	11 453.0	11 581.7	300	He	1.24	338
	11580p	11 580.0	11 628.3	300	He	1.24	338
	12750p	12 750.0	12 792.6	300	He	1.24	338

	13415	13 415.0	13 426.1	350	He	1.24	338
	13415_cont	13 426.0	13 493.5	350	He	1.24	338
	14070p	14 070.0	14 274.3	350	He	1.24	338
	7700p	7700.0	7741.58	500	Ne	1.24	298
	7730p	7730.0	8033.6	500	He	1.24	298
	8010p	8010.0	8273.68	150	He	1.38	298
pentafluoroiodobenzene	8274p	8274.0	8634.0	150	He	1.03	298
	8698p	8698.0	8830.53	150	He	1.03	298
	8830p	8830.53	9260.43	150	He	1.03	298
	9435p	9435.0	9955.29	150	He	1.03	298

2 Extended Townes-Dailey Model

2.1 Tables

Tab. S11: Results for the ionic characters I_{TD} and valence p orbital occupations n_x, n_y and n_z of the fluoroiodobenzenes and iodobenzene, following the implementation of the extended Townes-Dailey model, as described in Sec. 2.4 of the main text. The nomenclature of the molecules in the left-hand column is explained in Fig. 1 of the main text.

Molecule	I_{TD} / %	n_z	n_y	n_x
0	14.62(1)	1.165	2.000	1.981
2	6.49(2)	1.102	2.000	1.963
3	12.593(9)	1.148	2.000	1.978
4	13.9(3)	1.154	2.000	1.985
23	5.046(8)	1.089	2.000	1.962
24	6.09(2)	1.093	2.000	1.968
25	4.653(6)	1.087	2.000	1.960
26	−1.468(2)	1.041	2.000	1.944
34	12.07(3)	1.138	2.000	1.982
35	10.50(2)	1.130	2.000	1.975
234	4.87(1)	1.081	2.000	1.967
235	3.064(6)	1.072	2.000	1.959
236	−2.65(2)	1.029	2.000	1.944
245	4.37(2)	1.079	2.000	1.965
246	−1.703(5)	1.033	2.000	1.950
345	10.1(3)	1.121	2.000	1.980
2345	2.917(8)	1.065	2.000	1.964
2346	−2.854(3)	1.022	2.000	1.950
2356	−4.156(5)	1.015	2.000	1.943
23456	−4.351(3)	1.008	2.000	1.949

Eq. 1 shows the unique solution of the valence p orbital occupations n_x, and n_z, following the implementation of the extended Townes-Dailey model, obtained by explicitly setting $n_y = 2$.

$$\begin{aligned} n_z &= \frac{2}{3}\left(\frac{\chi_{xx} - \chi_{yy}}{\chi_0}\right) \\ n_x &= -\frac{2}{3}\left(\frac{\chi_{xx} + 2\chi_{yy}}{\chi_0}\right) \end{aligned} \tag{1}$$

Tab. S12: Results for the ionic characters I_{TD} and the valence p orbital occupations n_x and n_z of the fluoroiodobenzenes and iodobenzene, obtained using the extended Townes-Dailey model by explicitly setting $n_y = 2$. The occupations were calculated according to Eq. 1, with the uncertainties resulting from a Gaussian error propagation. The nomenclature of the molecules in the left-hand column is explained in Fig. 1 of the main text.

Molecule	I_{TD} / %	n_z	n_x
0	14.614 70(91)	1.078 580(4)	1.965 146(6)
2	6.493 06(63)	1.086 619(3)	1.959 911(4)
3	12.592 53(35)	1.081 405(2)	1.967 260(2)
4	13.8487(50)	1.064 748(37)	1.964 419(34)
23	5.045 12(39)	1.088 771(2)	1.961 680(2)
24	6.091 09(44)	1.093 240(2)	1.967 671(3)
25	4.6530(15)	1.102 354(6)	1.962 577(9)
26	−1.468 35(32)	1.041 010(2)	1.944 307(2)
34	12.0736(31)	1.121 267(18)	1.979 742(17)
35	10.501 71(61)	1.071 827(4)	1.958 817(3)
234	4.866 51(44)	1.129 680(2)	1.975 338(3)
235	3.0644(16)	1.138 344(9)	1.982 392(9)
236	−2.6535(59)	1.147 713(31)	1.978 212(34)
245	4.3726(12)	1.165 221(6)	1.980 924(7)
246	−1.7047(19)	1.032 923(9)	1.950 029(11)
345	10.1009(80)	1.029 420(51)	1.944 045(41)
2345	2.916 68(21)	1.153 708 5(13)	1.984 778 4(16)
2346	−2.853 76(21)	1.165 221 3(15)	1.980 924 4(16)
2356	−4.1571(20)	1.015 329(12)	1.943 100(10)
23456	−4.351 91(63)	1.007 648(3)	1.948 833(4)

Tab. S13: Results for the ionic characters I_{TD} and the valence p orbital occupations n_x, n_y and n_z of the fluoroiodobenzenes and iodobenzene, following the implementation of the extended Townes-Dailey model, as described in Sec. 2.4 of the main text, and ionic characters obtained from an intrinsic basis bonding analysis (IBBA) at the B3LYP-D3(BJ,abc)/cc-pVTZ-DK level of theory with (I_{DKH2}) and without (I_{non}) the treatment of relativistic effects using DKH2, as described in Sec. 2.3 of the main text. Structures have been optimised at the B3LYP-D3(BJ,abc)/ma-def2-TZVP level of theory. The nomenclature of the molecules in the left-hand column is explained in Fig. 1 of the main text.

Molecule	I_{TD} / %	I_{non} / %	I_{DKH2} / %
0	14.62(1)	21.190	21.116
2	6.49(2)	19.360	19.025
3	12.593(9)	19.772	19.599
4	13.9(3)	20.624	20.506
23	5.046(8)	18.208	17.750
24	6.09(2)	18.868	18.496
25	4.653(6)	18.024	17.587
26	−1.468(2)	17.670	17.047
34	12.07(3)	19.392	19.178
35	10.50(2)	18.339	18.069
234	4.87(1)	17.830	17.336
235	3.064(6)	16.843	16.280
236	−2.65(2)	16.526	15.785
245	4.37(2)	17.698	17.225
246	−1.703(5)	17.237	16.577
345	10.1(3)	18.102	17.787
2345	2.917(8)	16.603	15.995
2346	−2.854(3)	16.207	15.423
2356	−4.156(5)	15.361	14.490
23456	−4.351(3)	15.135	14.205

Tab. S14: Results for the valence p orbital occupations n_x, n_y and n_z of the fluoroiodobenzenes and iodobenzene, obtained from the implementation of the extended Townes-Dailey model, as described in Sec. 2.4 of the main text and the results for the 5p orbital occupations, obtained from an intrinsic basis bonding analysis (IBBA) at the B3LYP-D3(BJ,abc)/cc-pVTZ-DK level of theory with ($n_{x,\mathrm{DKH}}$, $n_{y,\mathrm{DKH}}$ and $n_{z,\mathrm{DKH}}$) and without ($n_{y,\mathrm{non}}$, $n_{y,\mathrm{non}}$ and $n_{z,\mathrm{non}}$) the treatment of relativistic effects using DKH2, as described in Sec. 2.3 of the main text. To obtain the valence orbital occupations within the framework of an isolated iodine atom, the number of electrons of a specific orbital type was summed up and then assigned to the orbitals in accordance with the Aufbau principle. The structures were optimised at the B3LYP-D3(BJ,abc)/ma-def2-TZVP level of theory. The nomenclature of the molecules in the left-hand column is explained in Fig. 1 of the main text.

Molecule	n_x	n_y	n_z	$n_{x,\mathrm{non}}$	$n_{y,\mathrm{non}}$	$n_{z,\mathrm{non}}$	$n_{x,\mathrm{DKH2}}$	$n_{y,\mathrm{DKH2}}$	$n_{z,\mathrm{DKH2}}$
0	1.981	2.000	1.165	1.970	1.992	1.295	1.966	1.992	1.185
2	1.963	2.000	1.102	1.967	1.992	1.277	1.962	1.992	1.159
3	1.978	2.000	1.148	1.968	1.967	1.309	1.963	1.964	1.201
4	1.985	2.000	1.154	1.972	1.991	1.288	1.967	1.992	1.176
23	1.962	2.000	1.089	1.965	1.959	1.301	1.960	1.953	1.188
24	1.968	2.000	1.093	1.969	1.993	1.268	1.964	1.993	1.150
25	1.960	2.000	1.087	1.965	1.967	1.292	1.960	1.962	1.178
26	1.944	2.000	1.041	1.964	1.997	1.256	1.959	1.997	1.131
34	1.982	2.000	1.138	1.969	1.981	1.288	1.965	1.980	1.177
35	1.975	2.000	1.130	1.966	1.991	1.274	1.961	1.991	1.161
234	1.967	2.000	1.081	1.967	1.982	1.272	1.963	1.980	1.154
235	1.959	2.000	1.072	1.963	1.993	1.257	1.958	1.993	1.136
236	1.944	2.000	1.029	1.962	1.952	1.291	1.957	1.945	1.173
245	1.965	2.000	1.079	1.966	1.980	1.272	1.962	1.979	1.155
246	1.950	2.000	1.033	1.966	1.996	1.249	1.962	1.996	1.124
345	1.980	2.000	1.121	1.967	1.991	1.269	1.963	1.991	1.155
2345	1.964	2.000	1.065	1.965	1.992	1.252	1.960	1.992	1.131
2346	1.950	2.000	1.022	1.964	1.980	1.257	1.960	1.978	1.133
2356	1.943	2.000	1.015	1.960	1.995	1.240	1.955	1.995	1.112
23456	1.949	2.000	1.008	1.962	1.994	1.235	1.958	1.994	1.106

Tab. S15: The differences in deviations $\Delta(\Delta n_{\text{theo}})$ of the iodine atom's orbital occupations, Δn_{theo}, to the isolated iodine atom (10 electrons in s orbitals, 23 electrons in p orbitals, 20 electrons in d orbitals), for the fluoroiodobenzenes and iodobenzene from an intrinsic basis bonding analysis (IBBA), performed at the B3LYP-D3(BJ,abc)/cc-pVTZ-DK level of theory with versus without the treatment of relativistic effects using DKH2. Results without relativistic treatments were subtracted from those with DKH2 enabled. In all cases, absolute deviations were larger for the treatment of relativistic effects. A positive sign indicates a gain in electron density. Structures have been optimised at the B3LYP-D3(BJ,abc)/ma-def2-TZVP level of theory. Following the nomenclature from Fig. 1 of the main text, the data for all different substitution patterns is shown.

Molecule	$\Delta(\Delta n_{\text{theo,s}})$	$\Delta(\Delta n_{\text{theo,p}})$	$\Delta(\Delta n_{\text{theo,d}})$
0	0.125	−0.115	−0.011
2	0.130	−0.122	−0.011
3	0.126	−0.116	−0.011
4	0.126	−0.116	−0.011
23	0.130	−0.124	−0.012
24	0.131	−0.123	−0.012
25	0.131	−0.124	−0.011
26	0.135	−0.129	−0.012
34	0.126	−0.117	−0.011
35	0.127	−0.118	−0.011
234	0.131	−0.124	−0.012
235	0.131	−0.125	−0.012
236	0.135	−0.131	−0.012
245	0.131	−0.124	−0.012
246	0.135	−0.130	−0.012
345	0.127	−0.119	−0.011
2345	0.131	−0.125	−0.012
2346	0.135	−0.131	−0.012
2356	0.135	−0.132	−0.012
23456	0.135	−0.132	−0.012

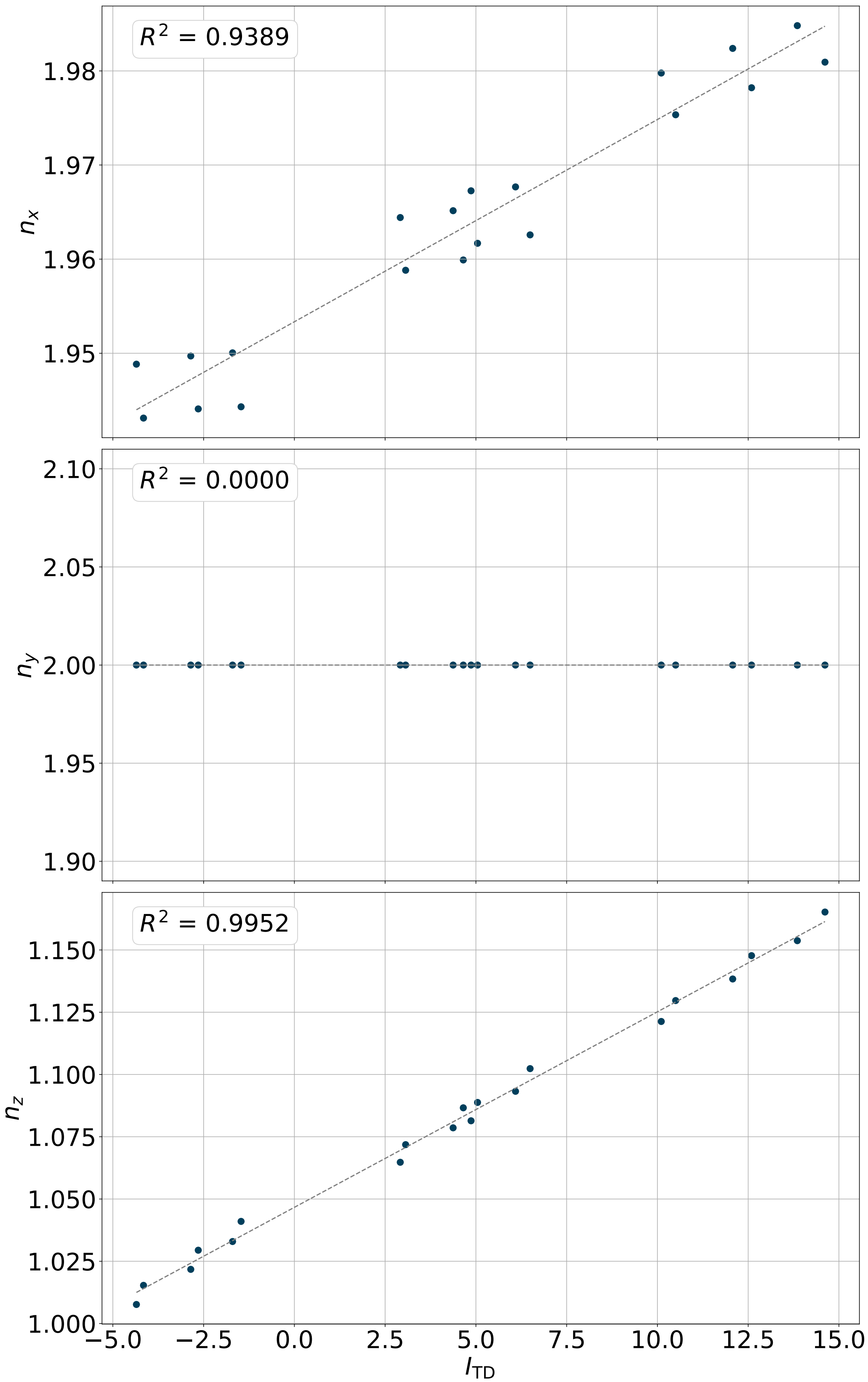

Fig. S1: The results of the valence p-orbital occupations n_x, n_y, and n_z of the fluoroiodobenzenes and iodobenzene plotted against their respective ionic characters I_{TD}. These values were obtained following the implementation of the extended Townes–Dailey model, as described in Section 2.4 of the main text. Linear trends are indicated by dashed lines and quantified by the R^2 values.

2.2 Figures

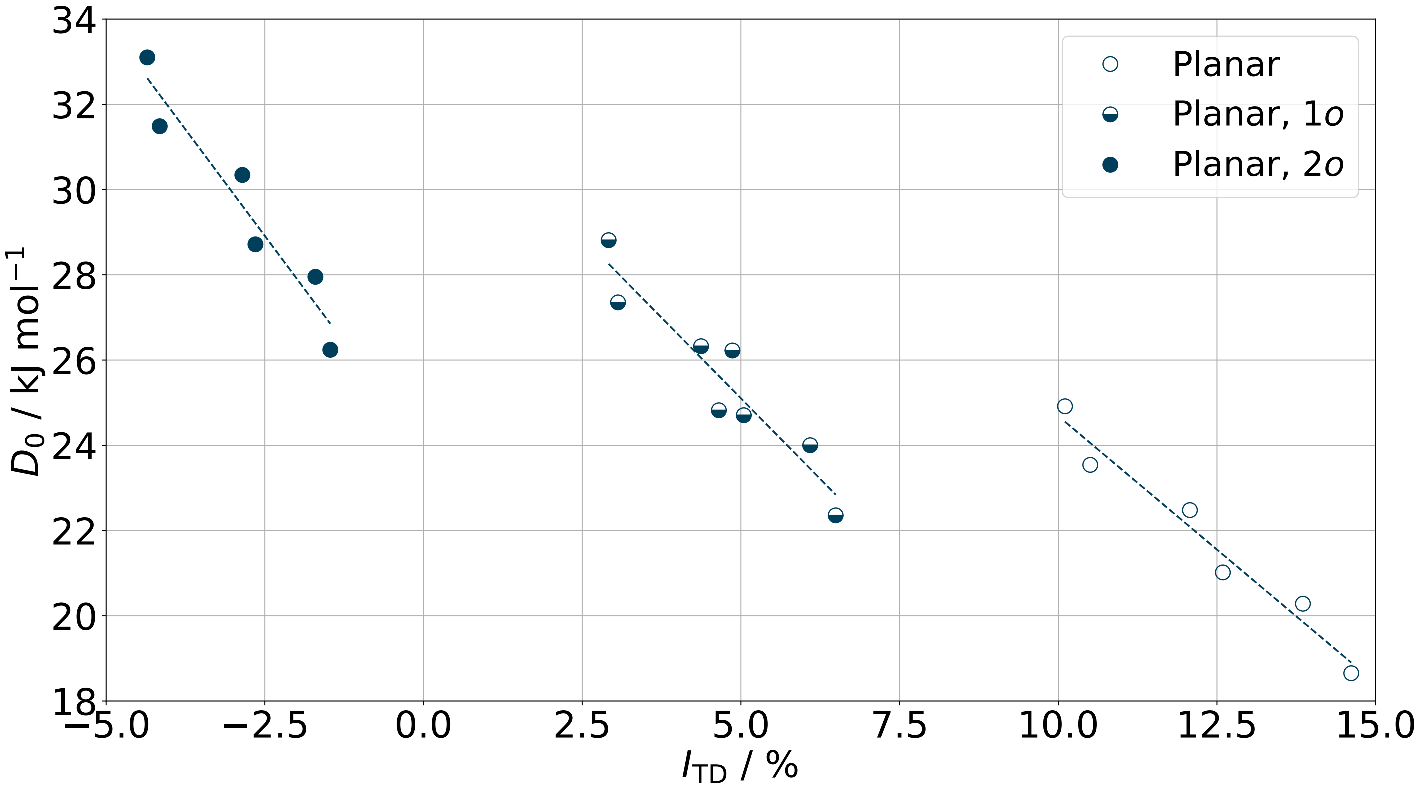

Fig. S2: Calculated zero-point-corrected dissociation energies D_0 of the planar halogen-bonded complexes of pyridine with the fluoroiodobenzenes, including iodobenzene, plotted against ionic characters I_{TD} following the implementation of the extended Townes-Dailey model. Calculations were performed at the B3LYP-D3(BJ,abc)/ma-def2-TZVP level of theory. Full circles represent two *ortho*-positioned fluorine atoms, half-filled circles represent one *ortho*-positioned fluorine atom, and empty circles represent an absence of *ortho*-positioned fluorine atoms. Dashed lines indicate linear trends and are discussed in the text. Exact values are summarised in Tab. S11 and Tab. S18.

3 Benchmarking Rotational Constants

3.1 Figures

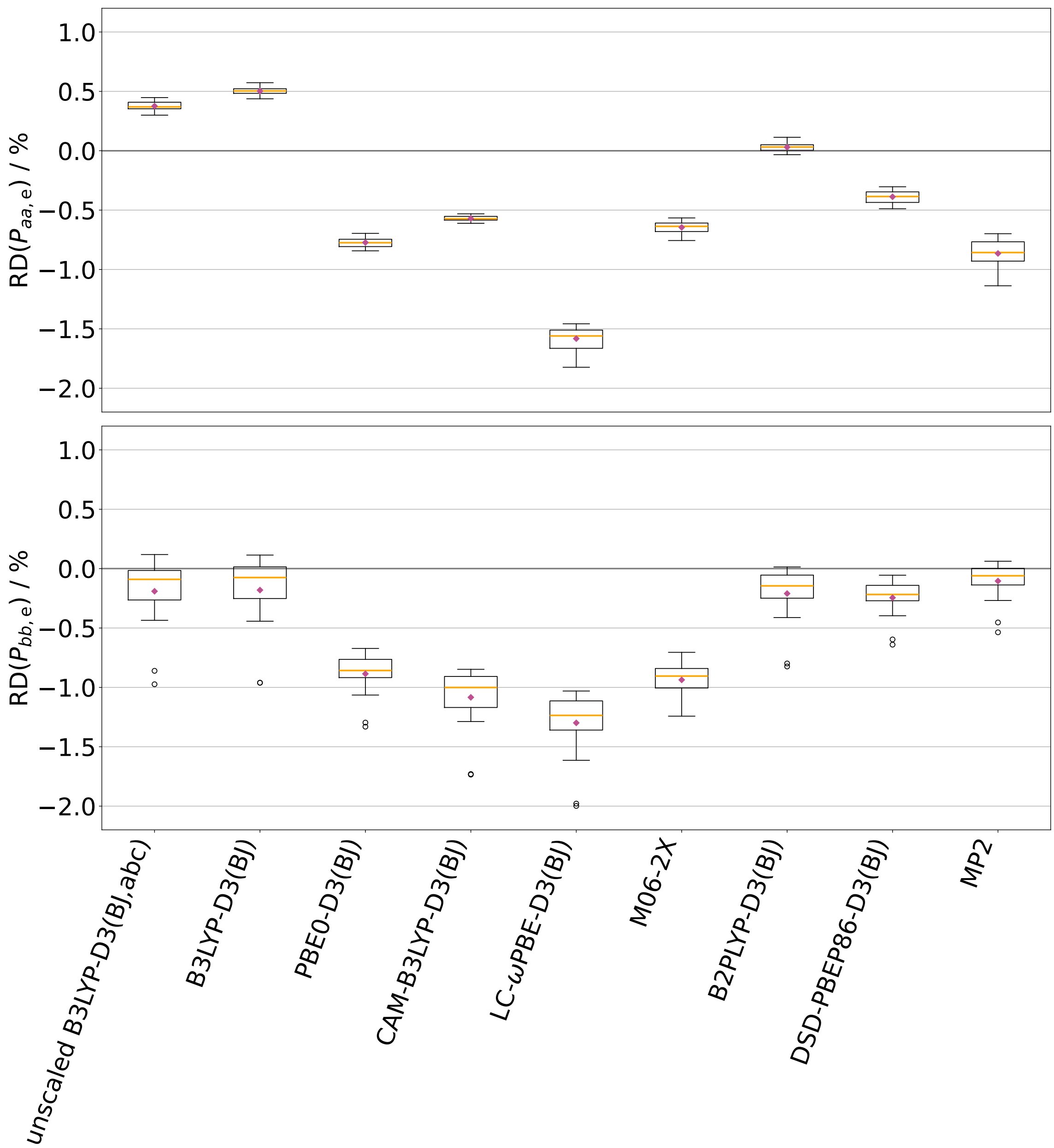

Fig. S3: Boxplots showing the three relative deviations RD($P_{aa,\mathrm{e}}$) and RD($P_{cc,\mathrm{e}}$) of the results of quantum chemical calculations from the experimental results for the planar moments. The RD of the individual planar moments is defined according to Eq. 6. The equilibrium planar moments $P_{aa,\mathrm{e}}$, $P_{bb,\mathrm{e}}$ and $P_{cc,\mathrm{e}}$ were obtained employing the functionals on the abscissa and utilising the def2-TZVP basis set. Details of the functionals used are given in Sec. 2.3. The orange line in a box represents the median of a group of values. The position of the averages is indicated by purple symbols. Boxes extend from the first quartile to the third quartile. Maximum whisker lengths extend to the first/third quartile minus/plus one and a half times the height of the box. Fliers are indicated with dots. Exact values can be found in Tab. S17.

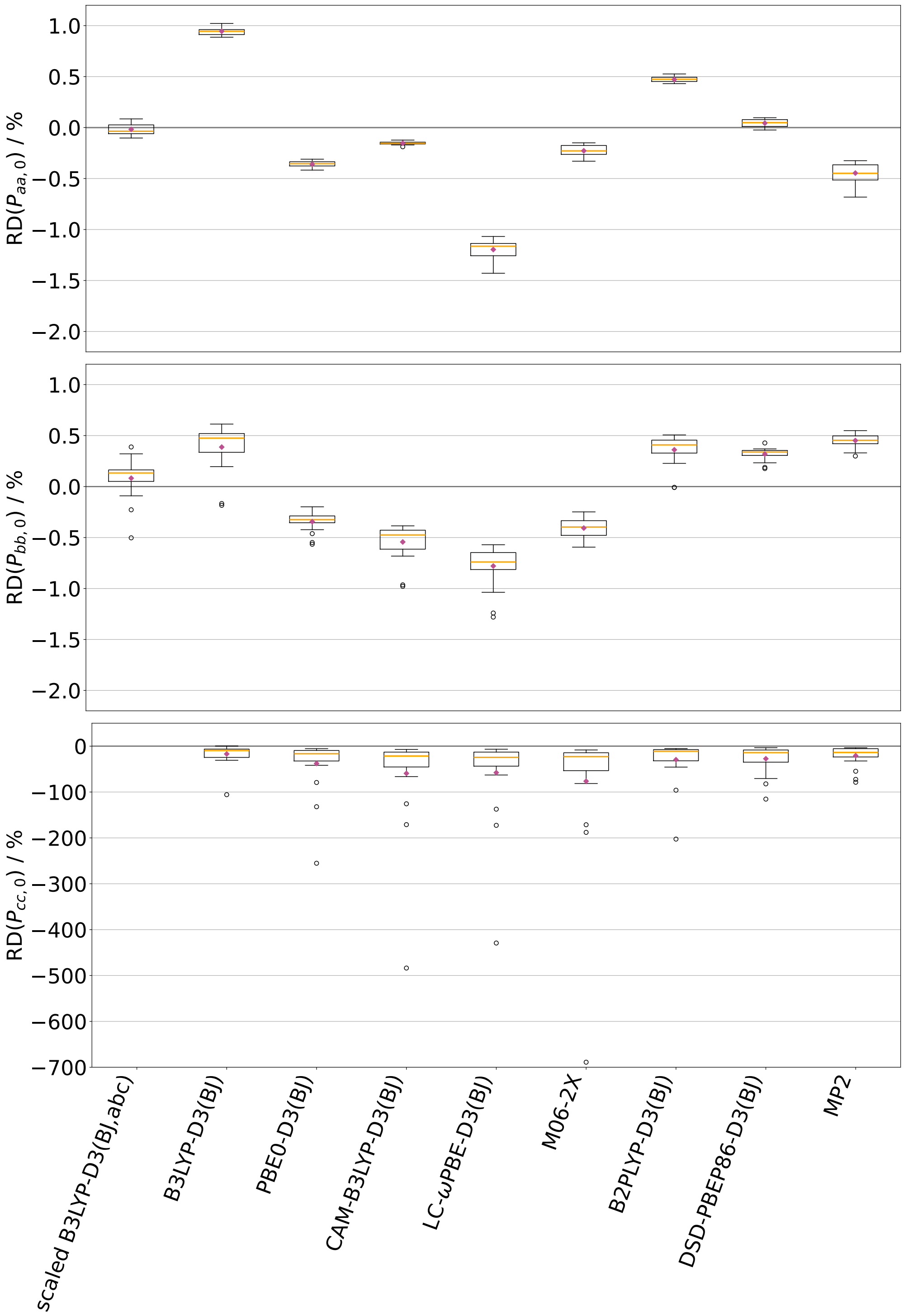

Fig. S4: Boxplots showing the three relative deviations RD($P_{aa,0}$) and RD($P_{cc,0}$), and RD($P_{cc,0}$) of the zero-point-corrected results of quantum chemical calculations from the experimental results for the planar moments. The RD of the individual planar moments is defined according to Eq. 6. results were obtained employing the functionals on the abscissa and utilising the def2-TZVP basis set. Details of the functionals used are given in Sec. 2.3. One exception to this is the method labelled with "scaled B3LYP-D3(BJ,abc)". In this case, an experimental training set was used to scale the calculated zero-point-corrected rotational constants obtained from a geometry optimisation at the B3LYP-D3(BJ,abc)/ma-def2-TZVP of theory without a VPT2 calculation. This level of theory has a self-referencing problem due to the inclusion of its training set into the testing set, as discussed in the main text. Given the large values obtained for RD($P_{cc,0}$) using the scaled approach, the respective box is not shown as this would significantly reduce the details of the remaining boxes. Exact values can be found in Tab. S17. The orange line in a box represents the median of a group of values. The position of the averages is indicated by purple symbols. Boxes extend from the first quartile to the third quartile. Maximum whisker lengths extend to the first/third quartile minus/plus one and a half times the height of the box. Fliers are indicated with dots.

3.2 Tables

All values are given in percent.

: Relative deviations (RD) of the quantum chemical calculation results from the experimental results for the equilibrium rotational constants A_e, B_e, C_e as well as their zero-point-corrected counterparts A_0, B_0, C_0. The individual RDs are defined according to Eq. 6 of the main text. The nomenclature follows Fig. 1 of the main text. The zero-point corrected rotational constants were obtained from VPT2 calculations, employing the functionals on the abscissa and utilising the def2-TZVP basis set. Details of the functionals used are given in Sec. 2.3 of the main text. One exception to this is the method labelled with "scaled B3LYP-D3(BJ,abc)". In this case, an experimental training set was used to scale the calculated zero-point-corrected rotational constants obtained from a geometry optimisation at the B3LYP-D3(BJ,abc)/ma-def2-TZVP of theory without a VPT2 calculation. This procedure is described in Sec. 2.3 of the main text. This level of theory has a self-referencing problem due to the inclusion of its training set into the testing set, as discussed in the main text.

Method	Molecule	RD(A_e)	RD(B_e)	RD(C_e)	RD(A_0)	RD(B_0)	RD(C_0)
	0	0.946	−0.418	−0.252	0.710	−0.027	0.012
	2	0.214	−0.426	−0.281	−0.020	−0.034	−0.017
	3	0.400	−0.380	−0.255	0.165	0.012	0.008
	4	0.756	−0.432	−0.324	0.756	−0.041	−0.060
	23	0.322	−0.450	−0.292	0.087	−0.059	−0.028
	24	0.206	−0.418	−0.325	−0.029	−0.026	−0.061
	25	−0.146	−0.307	−0.258	−0.380	0.085	0.006
	26	0.042	−0.397	−0.258	−0.193	−0.005	0.006
	34	0.301	−0.379	−0.295	0.066	0.013	−0.031
scaled	35	0.119	−0.364	−0.249	−0.116	0.027	0.015
B3LYP-D3(BJ,abc)	234	0.187	−0.406	−0.307	−0.048	−0.014	−0.044
	235	0.001	−0.367	−0.260	−0.233	0.025	0.004
	236	0.021	−0.366	−0.254	−0.213	0.026	0.010
	245	−0.124	−0.324	−0.283	−0.358	0.068	−0.020
	246	0.071	−0.397	−0.296	−0.163	−0.006	−0.033
	345	0.091	−0.351	−0.269	−0.144	0.041	−0.006
	2345	−0.023	−0.340	−0.268	−0.257	0.052	−0.004
	2346	0.008	−0.354	−0.271	−0.226	0.038	−0.008
	2356	0.017	−0.366	−0.239	−0.217	0.026	0.025
	23456	0.008	−0.337	−0.246	−0.226	0.055	0.018
	0	0.932	−0.548	−0.368	0.189	−1.000	−0.864
	2	0.200	−0.549	−0.382	−0.336	−0.993	−0.859
	3	0.408	−0.519	−0.373	−0.193	−0.951	−0.841
	4	0.977	−0.546	−0.430	0.172	−0.955	−0.869
	23	0.295	−0.574	−0.397	−0.268	−1.011	−0.866
	24	0.192	−0.526	−0.419	−0.377	−0.944	−0.863
	25	−0.142	−0.444	−0.363	−0.582	−0.903	−0.831
	26	0.009	−0.517	−0.352	−0.506	−0.972	−0.836
	34	0.307	−0.506	−0.407	−0.321	−0.916	−0.846
B3LYP-D3(BJ)	35	0.120	−0.511	−0.363	−0.397	−0.929	−0.816
	234	0.163	−0.519	−0.406	−0.393	−0.934	−0.846
	235	−0.017	−0.504	−0.365	−0.489	−0.919	−0.805
	236	−0.009	−0.490	−0.352	−0.514	−0.945	−0.828
	245	−0.125	−0.449	−0.386	−0.609	−0.878	−0.830
	246	0.035	−0.501	−0.386	−0.513	−0.944	−0.853
	345	0.096	−0.490	−0.383	−0.455	−0.899	−0.823
	2345	−0.037	−0.468	−0.371	−0.528	−0.883	−0.806

	2346	−0.026	−0.466	−0.366	−0.538	−0.904	−0.822
	2356	−0.020	−0.495	−0.339	−0.498	−0.938	−0.798
	23456	−0.027	−0.455	−0.342	−0.521	−0.901	−0.801
	0	1.276	0.781	0.847	0.559	0.354	0.376
	2	0.870	0.779	0.811	0.349	0.356	0.353
	3	1.039	0.778	0.827	0.467	0.376	0.388
	4	1.354	0.701	0.751	0.576	0.312	0.331
	23	0.966	0.758	0.806	0.427	0.332	0.350
	24	0.898	0.711	0.742	0.338	0.321	0.323
	25	0.681	0.816	0.798	0.265	0.375	0.349
	26	0.800	0.826	0.830	0.302	0.385	0.360
	34	0.956	0.726	0.757	0.352	0.330	0.331
PBE0-D3(BJ)	35	0.874	0.803	0.831	0.380	0.396	0.392
	234	0.893	0.731	0.759	0.350	0.330	0.333
	235	0.760	0.816	0.810	0.309	0.419	0.389
	236	0.792	0.817	0.816	0.303	0.381	0.357
	245	0.664	0.756	0.744	0.201	0.355	0.326
	246	0.844	0.747	0.770	0.318	0.339	0.334
	345	0.867	0.749	0.774	0.338	0.354	0.350
	2345	0.758	0.771	0.771	0.283	0.370	0.350
	2346	0.770	0.776	0.775	0.274	0.356	0.337
	2356	0.748	0.846	0.820	0.291	0.411	0.373
	23456	0.758	0.804	0.792	0.284	0.378	0.353
	0	1.722	0.582	0.722	0.995	0.148	0.245
	2	1.150	0.570	0.703	0.629	0.147	0.244
	3	1.267	0.583	0.693	0.691	0.169	0.244
	4	1.771	0.535	0.629	0.983	0.141	0.205
	23	1.131	0.564	0.682	0.587	0.144	0.230
	24	1.171	0.543	0.637	0.620	0.142	0.210
	25	0.885	0.606	0.682	0.476	0.159	0.229
	26	0.964	0.567	0.694	0.464	0.124	0.222
	34	1.231	0.551	0.635	0.630	0.155	0.210
CAM-B3LYP-D3(BJ)	35	0.996	0.578	0.680	0.500	0.170	0.240
	234	1.077	0.555	0.642	0.533	0.154	0.215
	235	0.882	0.588	0.675	0.429	0.189	0.252
	236	0.912	0.586	0.682	0.428	0.142	0.218
	245	0.918	0.574	0.641	0.458	0.171	0.222
	246	0.993	0.549	0.645	0.465	0.142	0.209
	345	1.019	0.550	0.637	0.484	0.156	0.212
	2345	0.903	0.571	0.646	0.432	0.168	0.225
	2346	0.916	0.572	0.651	0.421	0.154	0.213
	2356	0.847	0.594	0.680	0.388	0.159	0.231
	23456	0.866	0.582	0.657	0.389	0.148	0.211
	0	2.001	1.852	1.878	1.306	1.451	1.432
	2	1.330	1.770	1.692	0.823	1.367	1.252
	3	1.603	1.701	1.697	1.053	1.318	1.277
	4	2.024	1.595	1.627	1.265	1.229	1.231
	23	1.414	1.581	1.556	0.892	1.178	1.121
	24	1.330	1.543	1.515	0.790	1.177	1.119
	25	1.113	1.687	1.569	0.724	1.267	1.141
	26	1.229	1.731	1.595	0.745	1.306	1.139
	34	1.408	1.560	1.546	0.831	1.190	1.146
LC-ωPBE-D3(BJ)	35	1.227	1.683	1.597	0.752	1.297	1.178

	234	1.223	1.492	1.450	0.694	1.112	1.042
	235	1.064	1.633	1.490	0.628	1.252	1.084
	236	1.243	1.578	1.491	0.777	1.156	1.048
	245	1.053	1.536	1.453	0.612	1.159	1.059
	246	1.259	1.510	1.458	0.751	1.122	1.041
	345	1.178	1.548	1.489	0.662	1.178	1.087
	2345	1.034	1.514	1.412	0.576	1.138	1.014
	2346	1.154	1.478	1.405	0.676	1.081	0.987
	2356	1.073	1.595	1.433	0.633	1.174	1.000
	23456	1.063	1.488	1.376	0.603	1.084	0.956
M06-2X	0	1.212	0.599	0.679	0.489	0.159	0.196
	2	1.041	0.667	0.758	0.521	0.234	0.291
	3	0.961	0.617	0.678	0.397	0.198	0.226
	4	1.264	0.572	0.625	0.490	0.171	0.195
	23	0.840	0.757	0.781	0.304	0.332	0.325
	24	1.099	0.618	0.691	0.565	0.220	0.268
	25	0.967	0.607	0.702	0.601	0.151	0.252
	26	0.857	0.689	0.749	0.368	0.246	0.280
	34	1.038	0.576	0.634	0.450	0.171	0.203
	35	0.830	0.617	0.676	0.340	0.204	0.233
	234	0.961	0.672	0.722	0.429	0.276	0.300
	235	0.801	0.687	0.726	0.358	0.296	0.312
	236	0.792	0.713	0.741	0.321	0.276	0.286
	245	0.990	0.583	0.661	0.547	0.178	0.244
	246	0.879	0.651	0.701	0.365	0.246	0.270
	345	0.920	0.566	0.633	0.407	0.169	0.209
	2345	0.883	0.627	0.686	0.432	0.226	0.270
	2346	0.817	0.667	0.702	0.332	0.261	0.275
	2356	0.701	0.743	0.735	0.251	0.314	0.293
	23456	0.754	0.682	0.701	0.289	0.252	0.260
B2PLYP-D3(BJ)	0	0.767	−0.043	0.060	0.013	−0.493	−0.435
	2	0.203	−0.024	0.036	−0.329	−0.474	−0.445
	3	0.377	−0.042	0.030	−0.225	−0.474	−0.439
	4	0.836	−0.113	−0.040	0.013	−0.523	−0.482
	23	0.270	−0.051	0.019	−0.294	−0.491	−0.453
	24	0.224	−0.085	−0.036	−0.352	−0.505	−0.484
	25	−0.033	0.013	0.016	−0.461	−0.453	−0.456
	26	0.065	0.025	0.048	−0.452	−0.435	−0.441
	34	0.326	−0.081	−0.029	−0.312	−0.490	−0.470
	35	0.160	−0.037	0.018	−0.360	−0.462	−0.441
	234	0.207	−0.065	−0.019	−0.355	−0.486	−0.465
	235	0.040	−0.011	0.012	−0.431	−0.428	−0.430
	236	0.062	0.013	0.033	−0.445	−0.445	−0.447
	245	−0.027	−0.036	−0.029	−0.502	−0.470	−0.477
	246	0.098	−0.045	−0.013	−0.456	−0.494	−0.487
	345	0.174	−0.066	−0.019	−0.380	−0.479	−0.463
	2345	0.050	−0.033	−0.012	−0.443	−0.451	−0.449
	2346	0.046	−0.016	−0.001	−0.471	−0.455	−0.459
	2356	0.026	0.020	0.028	−0.452	−0.434	−0.440
	23456	0.039	−0.001	0.010	−0.453	−0.443	−0.446
	0	0.563	0.437	0.460	−0.183	−0.004	−0.026
	2	0.193	0.440	0.402	−0.331	−0.003	−0.072
	3	0.361	0.400	0.406	−0.230	−0.026	−0.057

	4	0.650	0.305	0.331	−0.171	−0.090	−0.097
	23	0.289	0.382	0.371	−0.266	−0.055	−0.097
	24	0.232	0.316	0.308	−0.340	−0.096	−0.133
	25	0.048	0.435	0.360	−0.366	−0.024	−0.103
	26	0.163	0.483	0.400	−0.349	0.024	−0.087
	34	0.322	0.323	0.326	−0.305	−0.082	−0.109
DSD-PBEP86-D3(BJ)	35	0.218	0.406	0.378	−0.295	−0.013	−0.075
	234	0.242	0.329	0.317	−0.318	−0.083	−0.122
	235	0.108	0.422	0.347	−0.355	0.009	−0.089
	236	0.179	0.431	0.367	−0.320	−0.025	−0.108
	245	0.043	0.349	0.298	−0.423	−0.080	−0.143
	246	0.206	0.349	0.320	−0.341	−0.077	−0.134
	345	0.244	0.336	0.325	−0.307	−0.067	−0.110
	2345	0.129	0.358	0.311	−0.359	−0.055	−0.122
	2346	0.155	0.367	0.320	−0.356	−0.064	−0.131
	2356	0.119	0.450	0.350	−0.351	−0.005	−0.116
	23456	0.142	0.387	0.323	−0.344	−0.042	−0.122
	0	0.418	0.963	0.908	−0.328	0.536	0.434
	2	0.024	1.028	0.833	−0.480	0.586	0.363
	3	0.232	0.864	0.782	−0.354	0.458	0.338
	4	0.544	0.704	0.691	−0.294	0.327	0.278
	23	0.134	0.923	0.774	−0.407	0.489	0.311
	24	0.085	0.748	0.655	−0.494	0.349	0.225
	25	−0.023	0.917	0.714	−0.417	0.459	0.258
	26	−0.040	1.142	0.804	−0.541	0.687	0.323
	34	0.204	0.718	0.660	−0.415	0.326	0.237
MP2	35	0.055	0.857	0.696	−0.449	0.450	0.254
	234	0.119	0.776	0.670	−0.429	0.373	0.240
	235	−0.030	0.922	0.676	−0.485	0.511	0.243
	236	0.053	0.993	0.738	−0.446	0.546	0.269
	245	−0.075	0.756	0.609	−0.527	0.344	0.185
	246	0.002	0.828	0.654	−0.543	0.389	0.188
	345	0.118	0.731	0.629	−0.424	0.342	0.207
	2345	0.015	0.786	0.620	−0.452	0.380	0.196
	2346	−0.007	0.839	0.647	−0.511	0.412	0.200
	2356	−0.035	1.011	0.681	−0.494	0.560	0.222
	23456	0.000	0.865	0.635	−0.468	0.452	0.208

Tab. S17: Relative deviations (RD) of the quantum chemical calculation results from the experimental results for the equilibrium planar moments $P_{aa,\mathrm{e}}$, $P_{bb,\mathrm{e}}$, $P_{cc,\mathrm{e}}$ as well as their zero-point-corrected counterparts $P_{aa,0}$, $P_{bb,0}$, and $P_{cc,0}$. The individual RDs are defined according to Eq. 6 of the main text. The nomenclature follows Fig. 1 of the main text. The zero-point corrected planar moments were obtained from VPT2 calculations, employing the functionals on the abscissa and utilising the def2-TZVP basis set. Details of the functionals used are given in Sec. 2.3 of the main text. One exception to this is the method labelled with "scaled B3LYP-D3(BJ,abc)". In this case, an experimental training set was used to scale the calculated zero-point-corrected planar moments obtained from a geometry optimisation at the B3LYP-D3(BJ,abc)/ma-def2-TZVP of theory without a VPT2 calculation. This procedure is described in Sec. 2.3 of the main text. This level of theory has a self-referencing problem due to the inclusion of its training set into the testing set, as discussed in the main text. All values are given in percent.

Method	Molecule	RD($P_{aa,\mathrm{e}}$)	RD($P_{bb,\mathrm{e}}$)	RD($P_{aa,0}$)	RD($P_{bb,0}$)	RD($P_{cc,0}$)

scaled B3LYP-D3(BJ,abc)	0	0.415	−0.974	0.053	−0.503	−541.343
	2	0.419	−0.247	0.025	−0.014	104.252
	3	0.375	−0.435	0.003	−0.076	−239.260
	4	0.425	−0.861	0.085	−0.228	−10 211.703
	23	0.448	−0.339	0.058	−0.091	20.765
	24	0.418	−0.218	0.047	0.147	−963.847
	25	0.300	0.118	−0.103	0.321	211.999
	26	0.391	−0.061	−0.042	0.079	591.742
	34	0.378	−0.316	0.016	0.146	−1323.949
	35	0.358	−0.147	−0.039	0.072	151.052
	234	0.407	−0.192	0.029	0.120	−1222.191
	235	0.362	−0.018	−0.057	0.144	532.080
	236	0.363	−0.032	−0.060	0.122	846.265
	245	0.322	0.112	−0.062	0.389	−228.509
	246	0.398	−0.076	0.002	0.149	325.915
	345	0.349	−0.106	−0.032	0.185	−272.611
	2345	0.339	0.016	−0.060	0.232	356.980
	2346	0.355	−0.009	−0.047	0.195	1839.640
	2356	0.363	−0.026	−0.082	0.097	1414.852
	23456	0.338	−0.009	−0.080	0.156	19 809.088
B3LYP-D3(BJ)	0	0.546	−0.961	1.011	−0.184	−12.489
	2	0.544	−0.232	1.003	0.340	−8.983
	3	0.515	−0.443	0.960	0.196	−6.924
	4	0.549	−0.962	0.965	−0.166	−105.803
	23	0.573	−0.312	1.022	0.269	−3.468
	24	0.527	−0.204	0.953	0.382	−26.422
	25	0.437	0.114	0.912	0.587	−5.996
	26	0.512	−0.028	0.982	0.509	−6.641
	34	0.507	−0.322	0.925	0.323	−7.330
	35	0.505	−0.148	0.938	0.399	−3.833
	234	0.521	−0.169	0.943	0.395	−13.956
	235	0.500	0.000	0.927	0.492	−3.185
	236	0.489	−0.002	0.955	0.519	−24.639
	245	0.448	0.112	0.886	0.613	−8.170
	246	0.502	−0.040	0.954	0.517	−30.759
	345	0.489	−0.111	0.908	0.459	−10.054
	2345	0.468	0.029	0.891	0.531	−11.646
	2346	0.468	0.024	0.913	0.541	−26.030
	2356	0.493	0.011	0.947	0.500	0.358
	23456	0.457	0.027	0.909	0.523	−24.513
PBE0-D3(BJ)	0	−0.779	−1.297	−0.352	−0.549	−17.085
	2	−0.781	−0.895	−0.354	−0.344	−10.923
	3	−0.778	−1.065	−0.374	−0.462	−7.972
	4	−0.696	−1.331	−0.310	−0.566	−132.081
	23	−0.757	−0.975	−0.330	−0.423	−10.048
	24	−0.708	−0.903	−0.320	−0.333	−32.138
	25	−0.818	−0.704	−0.373	−0.262	−9.034
	26	−0.828	−0.813	−0.383	−0.299	−9.684
	34	−0.723	−0.963	−0.328	−0.348	−20.169
	35	−0.804	−0.895	−0.394	−0.377	−5.584
	234	−0.727	−0.891	−0.329	−0.347	−30.212
	235	−0.815	−0.771	−0.417	−0.306	−7.482
	236	−0.815	−0.797	−0.378	−0.299	−33.016

	245	−0.753	−0.672	−0.353	−0.198	−15.852
	246	−0.743	−0.841	−0.337	−0.315	−41.771
	345	−0.746	−0.875	−0.352	−0.334	−17.735
	2345	−0.767	−0.759	−0.368	−0.281	−13.519
	2346	−0.771	−0.766	−0.355	−0.272	−79.216
	2356	−0.843	−0.751	−0.410	−0.290	−6.274
	23456	−0.798	−0.753	−0.376	−0.283	−255.256
CAM-B3LYP-D3(BJ)	0	−0.583	−1.730	−0.147	−0.979	−17.784
	2	−0.575	−1.169	−0.145	−0.621	−13.014
	3	−0.586	−1.288	−0.168	−0.682	−10.725
	4	−0.531	−1.735	−0.140	−0.965	−171.091
	23	−0.566	−1.136	−0.144	−0.581	−14.117
	24	−0.542	−1.170	−0.141	−0.612	−36.808
	25	−0.611	−0.905	−0.157	−0.471	−10.896
	26	−0.572	−0.973	−0.123	−0.459	−12.646
	34	−0.550	−1.232	−0.154	−0.623	−21.616
	35	−0.583	−1.015	−0.169	−0.495	−7.160
	234	−0.553	−1.071	−0.153	−0.526	−58.221
	235	−0.591	−0.891	−0.188	−0.425	−10.531
	236	−0.587	−0.915	−0.140	−0.422	−41.069
	245	−0.574	−0.922	−0.170	−0.452	−25.975
	246	−0.548	−0.987	−0.141	−0.459	−66.404
	345	−0.551	−1.024	−0.155	−0.478	−21.351
	2345	−0.570	−0.902	−0.168	−0.429	−24.551
	2346	−0.569	−0.909	−0.153	−0.417	−125.659
	2356	−0.594	−0.848	−0.159	−0.385	−13.580
	23456	−0.579	−0.859	−0.147	−0.386	−483.735
LC-ωPBE-D3(BJ)	0	−1.823	−1.998	−1.429	−1.280	−21.455
	2	−1.747	−1.345	−1.347	−0.812	−13.224
	3	−1.679	−1.614	−1.300	−1.037	−11.477
	4	−1.569	−1.979	−1.213	−1.241	−172.613
	23	−1.561	−1.412	−1.164	−0.881	−16.114
	24	−1.521	−1.325	−1.162	−0.778	−42.201
	25	−1.667	−1.129	−1.250	−0.716	−9.529
	26	−1.709	−1.233	−1.288	−0.737	−11.957
	34	−1.538	−1.404	−1.175	−0.818	−34.560
	35	−1.663	−1.240	−1.280	−0.744	−6.723
	234	−1.471	−1.214	−1.099	−0.686	−47.626
	235	−1.613	−1.070	−1.236	−0.622	−9.673
	236	−1.558	−1.238	−1.141	−0.767	−39.443
	245	−1.516	−1.055	−1.145	−0.605	−25.370
	246	−1.488	−1.248	−1.108	−0.742	−62.898
	345	−1.527	−1.179	−1.163	−0.654	−24.623
	2345	−1.493	−1.031	−1.124	−0.570	−24.213
	2346	−1.457	−1.142	−1.068	−0.670	−137.357
	2356	−1.574	−1.070	−1.160	−0.628	−14.010
	23456	−1.467	−1.052	−1.072	−0.598	−429.170
	0	−0.600	−1.235	−0.158	−0.478	−20.907
	2	−0.671	−1.063	−0.232	−0.514	−12.597
	3	−0.619	−0.989	−0.197	−0.391	−10.126
	4	−0.569	−1.243	−0.170	−0.479	−171.355
	23	−0.756	−0.851	−0.330	−0.300	−18.800
	24	−0.616	−1.100	−0.219	−0.556	−47.306

	25	−0.612	−0.986	−0.150	−0.594	−9.526
	26	−0.692	−0.868	−0.244	−0.363	−15.057
	34	−0.575	−1.044	−0.170	−0.444	−23.655
M06-2X	35	−0.621	−0.852	−0.203	−0.337	−8.348
	234	−0.669	−0.958	−0.275	−0.423	−71.760
	235	−0.688	−0.811	−0.295	−0.355	−11.954
	236	−0.712	−0.796	−0.273	−0.315	−47.019
	245	−0.582	−0.993	−0.177	−0.541	−25.935
	246	−0.648	−0.876	−0.245	−0.360	−81.526
	345	−0.566	−0.927	−0.168	−0.403	−18.663
	2345	−0.625	−0.883	−0.225	−0.428	−34.692
	2346	−0.663	−0.812	−0.259	−0.327	−187.956
	2356	−0.742	−0.705	−0.313	−0.249	−21.892
	23456	−0.677	−0.749	−0.250	−0.286	−688.919
	0	0.038	−0.799	0.496	−0.009	−11.836
	2	0.016	−0.235	0.477	0.333	−8.717
	3	0.036	−0.412	0.477	0.228	−6.843
	4	0.113	−0.824	0.526	−0.008	−95.991
	23	0.047	−0.287	0.494	0.297	−7.611
	24	0.083	−0.236	0.508	0.357	−31.666
	25	−0.022	0.005	0.456	0.465	−7.282
	26	−0.033	−0.084	0.437	0.455	−7.883
	34	0.079	−0.341	0.493	0.315	−16.453
B2PLYP-D3(BJ)	35	0.029	−0.188	0.464	0.363	−7.213
	234	0.064	−0.212	0.488	0.358	−20.753
	235	0.005	−0.057	0.431	0.434	−5.895
	236	−0.017	−0.072	0.448	0.451	−32.977
	245	0.033	0.014	0.473	0.507	−16.896
	246	0.044	−0.102	0.497	0.460	−45.669
	345	0.063	−0.188	0.482	0.383	−10.432
	2345	0.031	−0.057	0.453	0.445	−9.300
	2346	0.016	−0.048	0.457	0.474	−39.130
	2356	−0.024	−0.034	0.436	0.454	−5.305
	23456	0.000	−0.040	0.446	0.456	−202.591
	0	−0.440	−0.596	0.005	0.188	−12.342
	2	−0.446	−0.226	0.003	0.335	−8.438
	3	−0.405	−0.397	0.026	0.233	−8.296
	4	−0.303	−0.640	0.091	0.177	−115.445
	23	−0.385	−0.306	0.056	0.268	−8.471
	24	−0.317	−0.244	0.097	0.345	−38.096
	25	−0.442	−0.076	0.025	0.370	−8.480
	26	−0.489	−0.182	−0.024	0.352	−7.486
	34	−0.324	−0.337	0.082	0.308	−14.868
DSD-PBEP86-D3(BJ)	35	−0.412	−0.246	0.013	0.298	−6.174
	234	−0.329	−0.247	0.083	0.321	−33.866
	235	−0.426	−0.124	−0.008	0.358	−7.193
	236	−0.433	−0.189	0.026	0.325	−30.013
	245	−0.351	−0.056	0.081	0.428	−21.954
	246	−0.349	−0.210	0.077	0.344	−41.707
	345	−0.338	−0.259	0.068	0.310	−15.343
	2345	−0.358	−0.136	0.056	0.361	−13.296
	2346	−0.366	−0.157	0.065	0.358	−70.644
	2356	−0.452	−0.127	0.005	0.353	−3.490

	23456	−0.386	−0.143	0.042	0.346	−82.213
	0	−0.958	−0.453	−0.533	0.330	−3.648
	2	−1.026	−0.057	−0.582	0.484	−5.262
	3	−0.863	−0.268	−0.456	0.357	−4.882
	4	−0.699	−0.537	−0.326	0.299	−78.717
	23	−0.919	−0.152	−0.487	0.410	−4.113
	24	−0.745	−0.097	−0.348	0.500	−32.317
	25	−0.917	−0.005	−0.457	0.420	−6.765
	26	−1.137	0.021	−0.682	0.545	−6.251
	34	−0.715	−0.219	−0.325	0.420	−15.924
MP2	35	−0.857	−0.084	−0.447	0.453	−6.272
	234	−0.772	−0.124	−0.371	0.432	−21.050
	235	−0.920	0.013	−0.508	0.488	−5.660
	236	−0.988	−0.064	−0.542	0.452	−31.100
	245	−0.753	0.062	−0.342	0.532	−17.962
	246	−0.823	−0.006	−0.387	0.548	−54.706
	345	−0.729	−0.133	−0.340	0.428	−15.896
	2345	−0.782	−0.022	−0.378	0.455	−11.477
	2346	−0.833	0.006	−0.410	0.515	−72.437
	2356	−1.005	0.026	−0.556	0.496	−4.377
	23456	−0.857	0.000	−0.450	0.470	−16.585

Tab. S18: Zero-point-corrected dissociation energies D_0 of the planar complexes of the fluoroiodibenzenes/iodobenzene and pyridine. Structures were optimised at the B3LYP-D3(BJ,abc)/ma-def2-TZVP level of theory. The nomenclature follows Fig. 1 of the main text.

Molecule	D_0 / $\mathrm{kJ\,mol^{-1}}$
0	18.65
2	22.36
3	21.02
4	20.28
23	24.71
24	24.00
25	24.82
26	26.24
34	22.48
35	23.54
234	26.22
235	27.35
236	28.71
245	26.32
246	27.95
345	24.92
2345	28.81
2346	30.34
2356	31.49
23456	33.10

4 Benchmarking Nuclear Quadrupole Coupling Constants

4.1 Tables

Tab. S19: The relative deviations (RD) of the quantum chemical calculation results from the experimental results for the diagonal components of the nuclear quadrupole coupling tensor in the inertial principal axis system. The left column shows the raw results, whereas results in the right column were obtained by applying semi-experimental scaling. The individual RDs, RD(χ_{aa}), RD(χ_{bb}) and RD(χ_{cc}) are defined according to Eq. 6 of the main text. Values are tabulated for the fluoroiodobenzenes, iodobenzene, as well as for the molecules in Bailey's[8] original training set. All geometries were optimised at the B3LYP-D3(BJ,abc)/ma-def2-TZVP level of theory. The nomenclature for the fluoroiodobenzenes and iodobenzene is shown in Fig. 1 of the main text. Functionals are combined with the x2c-TZVPPall basis set, unless otherwise stated. In some cases, the basis set was decontracted. This is indicated by "d.". Additionally, "Bailey" describes the level of theory proposed by Bailey, as described in Sec. 2.3 of the main text, utilising the respective optimised nuclear quadrupole moments Q_{eff}. This level of theory has a self-referencing problem due to the inclusion of its training set into the testing set, as discussed in the main text. Details of the remaining functionals used are given in Sec. 2.3 of the main text. All values are given in percent.

Molecule	RD(χ_{aa})	RD(χ_{bb})	RD(χ_{cc})	RD(χ_{aa})	RD(χ_{bb})	RD(χ_{cc})
			PBE/def2-SVP			
0	98.236	−98.224	−98.250	0.547	0.516	−1.465
2	98.237	−98.236	−98.237	0.561	−0.187	−0.746
3	98.240	−98.222	−98.257	0.730	0.605	−1.841
4	98.234	−98.226	−98.243	0.434	0.384	−1.083
23	98.235	−98.230	−98.239	0.437	0.156	−0.836
24	98.235	−98.241	−98.229	0.459	−0.417	−0.274
25	98.242	−98.241	−98.243	0.855	−0.427	−1.093
26	98.236	−98.249	−98.220	0.522	−0.908	0.198
34	98.239	−98.227	−98.250	0.677	0.327	−1.502
35	98.241	−98.224	−98.260	0.819	0.531	−2.062
234	98.236	−98.240	−98.232	0.512	−0.373	−0.445
235	98.240	−98.238	−98.243	0.752	−0.272	−1.058
236	98.235	−98.248	−98.222	0.468	−0.864	0.114
245	98.240	−98.245	−98.236	0.767	−0.664	−0.666
246	98.234	−98.252	−98.211	0.383	−1.089	0.693
345	98.242	−98.230	−98.256	0.882	0.206	−1.830
2345	98.241	−98.245	−98.237	0.790	−0.645	−0.720
2346	98.235	−98.254	−98.214	0.457	−1.176	0.561
2356	98.238	−98.251	−98.221	0.611	−1.024	0.140
23456	98.237	−98.256	−98.214	0.561	−1.285	0.534
IF	98.236	−98.236	−98.236	0.499	−0.140	−0.667
HI	98.234	−98.234	−98.234	0.387	−0.028	−0.555
CH_3I	98.178	−98.178	−98.179	−2.724	3.095	2.551
CNI	98.270	−98.270	−98.270	2.428	−2.076	−2.592
C_2HI	98.294	−98.294	−98.294	3.789	−3.442	−3.951
CH_2I_2	98.067	−97.522	−98.142	−9.040	40.240	4.592
HOI	98.238	−98.259	−98.218	0.636	−1.475	0.355
C_3H_7I	98.174	−98.197	−98.146	−2.989	2.039	4.382
C_2H_5I	98.157	−98.138	−98.169	−3.933	5.414	3.078
CH_2ICl	98.162	−98.138	−98.171	−3.636	5.368	2.946
N_3I	98.149	−98.117	−98.161	−4.403	6.565	3.533
I_2	98.166	−98.166	−98.166	−3.445	3.818	3.271

C_2H_5OI	98.189	−98.165	−98.198	−2.131	3.832	1.460
C_2H_3I	98.243	−98.187	−98.292	0.930	2.585	−3.827
SiC_3H_9I	98.138	−98.138	−98.138	−5.025	5.406	4.847
OI_2	98.198	99.375	−98.321	−1.648	64.623	−5.459
			B3LYP-D3(BJ,abc)/d.			
0	11.247	−10.680	−11.854	0.535	−0.298	−0.703
2	11.405	−10.854	−12.028	0.712	−0.492	−0.900
3	11.330	−10.494	−12.144	0.629	−0.090	−1.030
4	11.232	−10.769	−11.721	0.519	−0.398	−0.553
23	11.329	−10.391	−12.264	0.628	0.024	−1.165
24	11.393	−10.964	−11.871	0.698	−0.615	−0.722
25	11.625	−10.924	−12.332	0.959	−0.570	−1.242
26	11.582	−11.025	−12.248	0.910	−0.683	−1.147
34	11.325	−10.668	−11.997	0.623	−0.285	−0.864
35	11.426	−10.549	−12.381	0.736	−0.152	−1.297
234	11.398	−10.741	−12.105	0.704	−0.366	−0.986
235	11.589	−10.773	−12.524	0.919	−0.402	−1.457
236	11.609	−10.729	−12.490	0.941	−0.352	−1.419
245	11.584	−11.036	−12.165	0.913	−0.695	−1.053
246	11.544	−11.093	−12.074	0.869	−0.759	−0.950
345	11.456	−10.704	−12.263	0.770	−0.325	−1.164
2345	11.598	−10.920	−12.358	0.929	−0.566	−1.271
2346	11.608	−10.982	−12.300	0.940	−0.635	−1.206
2356	11.727	−10.919	−12.694	1.074	−0.564	−1.650
23456	11.701	−11.020	−12.499	1.044	−0.678	−1.429
IF	9.012	−9.012	−9.012	−1.969	1.564	2.498
HI	10.673	−10.673	−10.673	−0.108	−0.290	0.628
CH_3I	10.612	−10.612	−10.612	−0.176	−0.222	0.696
CNI	12.650	−12.650	−12.650	2.107	−2.497	−1.599
C_2HI	12.604	−12.604	−12.604	2.056	−2.445	−1.548
CH_2I_2	5.597	27.083	−10.144	−5.796	41.854	1.223
HOI	9.735	−9.728	−9.742	−1.159	0.764	1.677
C_3H_7I	10.273	−11.220	−9.146	−0.556	−0.901	2.348
C_2H_5I	9.470	−7.826	−10.486	−1.456	2.888	0.838
CH_2ICl	8.358	−3.237	−10.310	−2.702	8.010	1.036
N_3I	5.638	3.201	−9.090	−5.751	15.196	2.411
I_2	9.884	−9.884	−9.884	−0.992	0.590	1.516
C_2H_5OI	9.998	−8.514	−10.558	−0.864	2.120	0.757
C_2H_3I	10.487	−7.579	−13.014	−0.317	3.164	−2.010
SiC_3H_9I	9.008	−9.006	−9.009	−1.974	1.570	2.502
OI_2	8.521	24.801	−10.225	−2.519	16.060	1.132
			B3LYP-D3(BJ,abc)-DKH2/d.			
0	−0.088	0.236	−0.070	0.256	−0.178	−0.286
2	0.082	−0.085	−0.079	0.426	−0.497	−0.295
3	0.011	0.388	−0.398	0.355	−0.027	−0.613
4	−0.102	0.136	0.066	0.242	−0.277	−0.150
23	0.043	0.266	−0.351	0.387	−0.148	−0.566
24	0.064	−0.179	0.065	0.408	−0.591	−0.152
25	0.263	−0.106	−0.422	0.606	−0.518	−0.637
26	0.249	−0.338	−0.142	0.592	−0.749	−0.358
34	0.022	0.201	−0.250	0.366	−0.213	−0.466
35	0.152	0.318	−0.664	0.496	−0.096	−0.879

234	0.119	−0.031	−0.214	0.462	−0.443	−0.429
235	0.317	−0.034	−0.642	0.660	−0.446	−0.857
236	0.267	−0.110	−0.424	0.610	−0.523	−0.639
245	0.257	−0.246	−0.268	0.600	−0.657	−0.484
246	0.220	−0.409	0.002	0.563	−0.820	−0.214
345	0.202	0.128	−0.556	0.545	−0.286	−0.771
2345	0.340	−0.198	−0.500	0.683	−0.610	−0.715
2346	0.304	−0.338	−0.266	0.647	−0.749	−0.482
2356	0.454	−0.280	−0.662	0.796	−0.691	−0.876
23456	0.447	−0.401	−0.501	0.789	−0.812	−0.716
IF	−0.919	0.919	0.919	−0.572	0.503	0.701
HI	−1.261	1.261	1.261	−0.912	0.843	1.042
CH_3I	−0.617	0.617	0.617	−0.271	0.202	0.399
CNI	1.312	−1.312	−1.312	1.652	−1.720	−1.526
C_2HI	0.909	−0.909	−0.909	1.250	−1.318	−1.123
CH_2I_2	−5.589	39.109	0.925	−5.225	38.535	0.706
HOI	−0.394	0.360	0.427	−0.048	−0.054	0.209
C_3H_7I	−0.837	−0.396	2.305	−0.490	−0.807	2.084
C_2H_5I	−1.861	3.704	0.722	−1.510	3.276	0.504
CH_2ICl	−2.624	7.883	0.620	−2.271	7.438	0.402
N_3I	−5.467	16.346	1.218	−5.104	15.866	0.999
I_2	−1.097	1.097	1.097	−0.749	0.679	0.878
C_2H_5OI	−1.206	2.909	0.564	−0.858	2.484	0.347
C_2H_3I	−0.983	3.969	−1.611	−0.636	3.540	−1.824
SiC_3H_9I	−3.848	3.850	3.846	−3.491	3.421	3.622
OI_2	−0.686	−28.430	3.588	−0.339	−27.900	3.364
B3LYP-D3(BJ,abc)-X2C/d.						
0	−0.590	0.754	0.413	0.235	−0.150	−0.276
2	−0.420	0.430	0.407	0.404	−0.471	−0.282
3	−0.488	0.903	0.084	0.336	−0.003	−0.603
4	−0.604	0.656	0.550	0.220	−0.248	−0.140
23	−0.453	0.774	0.133	0.371	−0.131	−0.554
24	−0.439	0.338	0.551	0.385	−0.563	−0.139
25	−0.239	0.414	0.063	0.582	−0.487	−0.624
26	−0.253	0.176	0.347	0.568	−0.724	−0.342
34	−0.477	0.716	0.232	0.347	−0.188	−0.456
35	−0.344	0.827	−0.183	0.479	−0.078	−0.868
234	−0.379	0.480	0.270	0.444	−0.422	−0.418
235	−0.179	0.475	−0.160	0.642	−0.427	−0.845
236	−0.232	0.402	0.062	0.590	−0.499	−0.625
245	−0.245	0.272	0.216	0.577	−0.628	−0.472
246	−0.282	0.105	0.490	0.540	−0.793	−0.200
345	−0.293	0.637	−0.075	0.529	−0.267	−0.761
2345	−0.156	0.311	−0.018	0.665	−0.590	−0.704
2346	−0.195	0.174	0.218	0.626	−0.726	−0.469
2356	−0.043	0.228	−0.178	0.777	−0.672	−0.864
23456	−0.050	0.108	−0.018	0.770	−0.791	−0.704
IF	−1.314	1.314	1.314	−0.484	0.405	0.619
HI	−1.809	1.809	1.809	−0.974	0.895	1.110
CH_3I	−1.066	1.066	1.065	−0.237	0.158	0.372
CNI	0.816	−0.816	−0.816	1.629	−1.707	−1.497
C_2HI	0.363	−0.363	−0.363	1.180	−1.258	−1.047
CH_2I_2	−6.051	39.719	1.366	−5.181	38.464	0.670

HOI	−0.808	0.770	0.845	0.018	−0.134	0.153
C_3H_7I	−1.329	0.077	2.820	−0.498	−0.822	2.114
C_2H_5I	−2.347	4.218	1.190	−1.508	3.282	0.496
CH_2ICl	−3.080	8.364	1.066	−2.235	7.391	0.372
N_3I	−5.922	16.846	1.656	−5.054	15.796	0.958
I_2	−1.508	1.508	1.508	−0.676	0.597	0.811
C_2H_5OI	−1.690	3.449	1.027	−0.857	2.520	0.334
C_2H_3I	−1.488	4.503	−1.133	−0.656	3.565	−1.811
SiC_3H_9I	−4.348	4.350	4.347	−3.493	3.413	3.630
OI_2	−1.346	−29.279	4.269	−0.516	−28.119	3.553
			Bailey			
0	1.870	0.262	−4.156	0.419	0.407	−1.701
2	2.002	0.195	−4.487	0.552	0.339	−2.040
3	2.022	0.429	−4.405	0.573	0.574	−1.956
4	1.747	0.230	−3.835	0.294	0.375	−1.371
23	1.889	0.823	−4.590	0.438	0.969	−2.146
24	1.932	0.024	−4.113	0.481	0.168	−1.656
25	2.420	−0.107	−4.752	0.976	0.038	−2.312
26	2.191	−0.046	−4.759	0.745	0.098	−2.319
34	1.964	0.171	−4.146	0.514	0.316	−1.690
35	2.064	0.194	−4.525	0.615	0.338	−2.079
234	1.990	0.141	−4.282	0.540	0.286	−1.830
235	2.232	−0.050	−4.733	0.786	0.094	−2.292
236	2.284	0.293	−4.861	0.839	0.438	−2.423
245	2.300	−0.286	−4.432	0.855	−0.142	−1.984
246	2.092	−0.148	−4.372	0.644	−0.004	−1.922
345	2.124	−0.034	−4.366	0.677	0.110	−1.916
2345	2.289	−0.338	−4.479	0.844	−0.194	−2.032
2346	2.250	−0.194	−4.525	0.804	−0.050	−2.079
2356	2.381	−0.317	−4.850	0.937	−0.173	−2.412
23456	2.370	−0.498	−4.564	0.926	−0.355	−2.119
IF	1.636	−1.636	−1.636	0.181	−1.494	0.884
HI	−1.389	1.389	1.389	−2.889	1.536	3.987
CH_3I	−0.459	0.459	0.459	−1.945	0.604	3.033
CNI	4.129	−4.129	−4.129	2.710	−3.990	−1.672
C_2HI	3.668	−3.668	−3.668	2.243	−3.529	−1.200
CH_2I_2	−5.802	40.143	1.024	−7.367	40.345	3.612
HOI	2.175	−2.355	−2.000	0.728	−2.214	0.511
C_3H_7I	−0.773	0.041	1.644	−2.264	0.186	4.249
C_2H_5I	−1.524	3.418	0.353	−3.026	3.568	2.924
CH_2ICl	−2.972	7.106	1.396	−4.495	7.261	3.994
N_3I	−2.894	11.954	−0.645	−4.416	12.116	1.901
I_2	−1.047	1.047	1.047	−2.542	1.193	3.636
C_2H_5OI	1.570	0.431	−2.323	0.113	0.576	0.179
C_2H_3I	1.370	3.366	−5.486	−0.089	3.515	−3.064
SiC_3H_9I	−4.117	4.119	4.115	−5.657	4.269	6.783
OI_2	0.706	−47.757	4.365	−0.763	−47.970	7.039
			B3LYP-D3(BJ,abc)			
0	−54.767	49.604	60.300	−3.770	2.692	5.219
2	−52.901	47.533	58.976	−2.519	1.270	4.350
3	−54.093	48.561	59.472	−3.318	1.976	4.676
4	−54.466	49.234	59.992	−3.569	2.438	5.017

23	−52.136	46.089	58.159	−2.006	0.279	3.814
24	−52.760	47.456	58.675	−2.425	1.218	4.152
25	−52.561	46.975	58.195	−2.291	0.887	3.837
26	−51.236	45.963	57.548	−1.403	0.193	3.413
34	−53.715	48.250	59.301	−3.065	1.763	4.563
35	−53.158	48.021	58.758	−2.691	1.605	4.207
234	−51.882	46.228	57.966	−1.836	0.375	3.687
235	−51.347	46.032	57.437	−1.477	0.240	3.340
236	−50.775	44.716	56.830	−1.094	−0.663	2.942
245	−52.158	46.630	58.010	−2.021	0.650	3.716
246	−51.068	45.825	57.218	−1.290	0.098	3.196
345	−52.780	47.342	58.612	−2.438	1.139	4.111
2345	−51.072	45.484	57.342	−1.293	−0.136	3.277
2346	−50.381	44.744	56.617	−0.829	−0.644	2.801
2356	−49.684	44.288	56.139	−0.362	−0.957	2.488
23456	−49.374	43.696	56.032	−0.154	−1.363	2.418
IF	−35.082	35.082	35.082	9.429	−7.276	−11.334
HI	−53.967	53.967	53.967	−3.234	5.687	1.062
CH_3I	−44.291	44.291	44.290	3.254	−0.955	−5.289
CNI	−48.493	48.493	48.493	0.437	1.929	−2.531
C_2HI	−56.873	56.873	56.873	−5.182	7.682	2.970
CH_2I_2	−51.619	106.476	43.986	−1.659	41.731	−5.489
HOI	−37.456	36.713	38.179	7.836	−6.157	−9.301
C_3H_7I	−50.990	46.750	56.041	−1.238	0.733	2.423
C_2H_5I	−50.470	55.192	47.552	−0.889	6.528	−3.149
CH_2ICl	−47.247	56.727	43.633	1.272	7.582	−5.721
N_3I	−46.353	58.555	41.587	1.872	8.836	−7.064
I_2	−33.408	33.408	33.408	10.551	−8.425	−12.433
C_2H_5OI	−48.874	53.727	47.045	0.181	5.522	−3.482
C_2H_3I	−53.778	55.176	52.563	−3.107	6.517	0.140
SiC_3H_9I	−52.947	52.948	52.945	−2.550	4.987	0.391
OI_2	−85.430	−27.785	79.398	−24.329	12.285	17.755
			B3LYP-D3(BJ,abc)-DKH			
0	−0.088	0.236	−0.070	0.256	−0.178	−0.286
2	0.082	−0.085	−0.079	0.426	−0.497	−0.295
3	0.011	0.388	−0.398	0.355	−0.027	−0.613
4	−0.102	0.136	0.066	0.242	−0.277	−0.150
23	0.043	0.266	−0.351	0.387	−0.148	−0.566
24	0.064	−0.179	0.065	0.408	−0.591	−0.152
25	0.263	−0.106	−0.422	0.606	−0.518	−0.637
26	0.249	−0.338	−0.142	0.592	−0.749	−0.358
34	0.022	0.201	−0.250	0.366	−0.213	−0.466
35	0.152	0.318	−0.664	0.496	−0.096	−0.879
234	0.119	−0.031	−0.214	0.462	−0.443	−0.429
235	0.317	−0.034	−0.642	0.660	−0.446	−0.857
236	0.267	−0.110	−0.424	0.610	−0.523	−0.639
245	0.257	−0.246	−0.268	0.600	−0.657	−0.484
246	0.220	−0.409	0.002	0.563	−0.820	−0.214
345	0.202	0.128	−0.556	0.545	−0.286	−0.771
2345	0.340	−0.198	−0.500	0.683	−0.610	−0.715
2346	0.304	−0.338	−0.266	0.647	−0.749	−0.482
2356	0.454	−0.280	−0.662	0.796	−0.691	−0.876
23456	0.447	−0.401	−0.501	0.789	−0.812	−0.716

IF	−0.919	0.919	0.919	−0.572	0.503	0.701
HI	−1.261	1.261	1.261	−0.912	0.843	1.042
CH_3I	−0.617	0.617	0.617	−0.271	0.202	0.399
CNI	1.312	−1.312	−1.312	1.652	−1.720	−1.526
C_2HI	0.909	−0.909	−0.909	1.250	−1.318	−1.123
CH_2I_2	−5.589	39.109	0.925	−5.225	38.535	0.706
HOI	−0.394	0.360	0.427	−0.048	−0.054	0.209
C_3H_7I	−0.837	−0.396	2.305	−0.490	−0.807	2.084
C_2H_5I	−1.861	3.704	0.722	−1.510	3.276	0.504
CH_2ICl	−2.624	7.883	0.620	−2.271	7.438	0.402
N_3I	−5.467	16.346	1.218	−5.104	15.866	0.999
I_2	−1.097	1.097	1.097	−0.749	0.679	0.878
C_2H_5OI	−1.206	2.909	0.564	−0.858	2.484	0.347
C_2H_3I	−0.983	3.969	−1.611	−0.636	3.540	−1.824
SiC_3H_9I	−3.848	3.850	3.846	−3.491	3.421	3.622
OI_2	−0.686	−28.430	3.588	−0.339	−27.900	3.364
B3LYP-D3(BJ,abc)-X2C						
0	−0.590	0.754	0.413	0.235	−0.150	−0.276
2	−0.420	0.430	0.407	0.404	−0.471	−0.282
3	−0.488	0.903	0.084	0.336	−0.003	−0.603
4	−0.604	0.656	0.550	0.220	−0.248	−0.140
23	−0.453	0.774	0.133	0.371	−0.131	−0.554
24	−0.439	0.338	0.551	0.385	−0.563	−0.139
25	−0.239	0.414	0.063	0.582	−0.487	−0.624
26	−0.253	0.176	0.347	0.568	−0.724	−0.342
34	−0.477	0.716	0.232	0.347	−0.188	−0.456
35	−0.344	0.827	−0.183	0.479	−0.078	−0.868
234	−0.379	0.480	0.270	0.444	−0.422	−0.418
235	−0.179	0.475	−0.160	0.642	−0.427	−0.845
236	−0.232	0.402	0.062	0.590	−0.499	−0.625
245	−0.245	0.272	0.216	0.577	−0.628	−0.472
246	−0.282	0.105	0.490	0.540	−0.793	−0.200
345	−0.293	0.637	−0.075	0.529	−0.267	−0.761
2345	−0.156	0.311	−0.018	0.665	−0.590	−0.704
2346	−0.195	0.174	0.218	0.626	−0.726	−0.469
2356	−0.043	0.228	−0.178	0.777	−0.672	−0.864
23456	−0.050	0.108	−0.018	0.770	−0.791	−0.704
IF	−1.314	1.314	1.314	−0.484	0.405	0.619
HI	−1.809	1.809	1.809	−0.974	0.895	1.110
CH_3I	−1.066	1.066	1.065	−0.237	0.158	0.372
CNI	0.816	−0.816	−0.816	1.629	−1.707	−1.497
C_2HI	0.363	−0.363	−0.363	1.180	−1.258	−1.047
CH_2I_2	−6.051	39.719	1.366	−5.181	38.464	0.670
HOI	−0.808	0.770	0.845	0.018	−0.134	0.153
C_3H_7I	−1.329	0.077	2.820	−0.498	−0.822	2.114
C_2H_5I	−2.347	4.218	1.190	−1.508	3.282	0.496
CH_2ICl	−3.080	8.364	1.066	−2.235	7.391	0.372
N_3I	−5.922	16.846	1.656	−5.054	15.796	0.958
I_2	−1.508	1.508	1.508	−0.676	0.597	0.811
C_2H_5OI	−1.690	3.449	1.027	−0.857	2.520	0.334
C_2H_3I	−1.488	4.503	−1.133	−0.656	3.565	−1.811
SiC_3H_9I	−4.348	4.350	4.347	−3.493	3.413	3.630
OI_2	−1.346	−29.279	4.269	−0.516	−28.119	3.553

			B2PLYP-D3(BJ,abc)			
0	−55.016	48.374	62.134	−3.371	1.857	5.675
2	−53.553	46.684	61.327	−2.396	0.697	5.149
3	−54.679	47.542	61.618	−3.147	1.286	5.339
4	−54.708	48.100	61.685	−3.166	1.669	5.383
23	−52.924	45.185	60.634	−1.977	−0.333	4.697
24	−53.447	46.804	60.856	−2.325	0.779	4.842
25	−53.659	46.534	60.843	−2.466	0.594	4.834
26	−52.228	45.501	60.281	−1.512	−0.116	4.468
34	−54.320	47.461	61.331	−2.907	1.230	5.152
35	−53.965	47.386	61.136	−2.670	1.179	5.025
234	−52.800	45.830	60.300	−1.894	0.111	4.480
235	−52.486	45.817	60.128	−1.684	0.101	4.368
236	−52.001	44.320	59.677	−1.361	−0.926	4.074
245	−53.235	46.373	60.498	−2.184	0.483	4.609
246	−52.085	45.528	59.778	−1.417	−0.097	4.139
345	−53.659	46.915	60.892	−2.466	0.855	4.866
2345	−52.305	45.542	59.893	−1.564	−0.087	4.215
2346	−51.652	44.730	59.310	−1.128	−0.645	3.834
2356	−51.084	44.455	59.012	−0.749	−0.834	3.640
23456	−50.827	44.061	58.760	−0.578	−1.104	3.476
IF	−37.326	37.326	37.326	8.425	−5.727	−10.494
HI	−52.819	52.819	52.819	−1.906	4.908	−0.396
CH_3I	−41.708	41.708	41.707	5.503	−2.719	−7.638
CNI	−51.335	51.335	51.335	−0.917	3.890	−1.363
C_2HI	−58.526	58.526	58.526	−5.712	8.826	3.323
CH_2I_2	−51.362	113.150	42.765	−0.935	46.325	−6.949
HOI	−38.620	38.007	39.216	7.562	−5.260	−9.262
C_3H_7I	−48.479	44.207	53.568	0.987	−1.004	0.092
C_2H_5I	−48.115	53.469	44.805	1.231	5.354	−5.619
CH_2ICl	−47.247	60.098	42.348	1.809	9.905	−7.221
N_3I	−47.765	60.341	42.853	1.464	10.072	−6.892
I_2	−34.086	34.086	34.086	10.585	−7.951	−12.606
C_2H_5OI	−48.190	55.261	45.526	1.180	6.585	−5.150
C_2H_3I	−54.366	53.127	55.442	−2.938	5.120	1.314
SiC_3H_9I	−49.474	49.476	49.473	0.324	2.613	−2.577
OI_2	−86.356	90.199	67.884	−24.270	93.272	9.423
			B2PLYP-D3(BJ,abc)-DKH			
0	−0.847	−0.150	1.915	0.759	−1.182	0.228
2	−1.011	−0.165	2.342	0.597	−1.196	0.647
3	−1.029	0.186	1.850	0.579	−0.849	0.163
4	−0.852	−0.171	1.933	0.753	−1.202	0.245
23	−1.157	0.129	2.181	0.454	−0.906	0.489
24	−1.060	−0.094	2.347	0.549	−1.126	0.652
25	−1.215	0.186	2.253	0.396	−0.849	0.559
26	−1.129	−0.104	2.605	0.481	−1.136	0.906
34	−1.035	0.186	1.903	0.574	−0.849	0.215
35	−1.077	0.431	1.782	0.532	−0.606	0.097
234	−1.195	0.257	2.205	0.416	−0.779	0.513
235	−1.190	0.419	2.075	0.420	−0.619	0.384
236	−1.308	0.188	2.428	0.305	−0.847	0.732
245	−1.202	0.187	2.276	0.409	−0.848	0.582
246	−1.180	−0.039	2.610	0.431	−1.072	0.911

345	−1.089	0.414	1.812	0.521	−0.623	0.126
2345	−1.247	0.482	2.106	0.364	−0.556	0.415
2346	−1.311	0.269	2.463	0.302	−0.766	0.766
2356	−1.272	0.478	2.221	0.341	−0.560	0.529
23456	−1.325	0.522	2.267	0.288	−0.516	0.574
IF	−3.399	3.399	3.399	−1.753	2.331	1.687
HI	−0.876	0.876	0.876	0.730	−0.166	−0.794
CH_3I	0.928	−0.928	−0.928	2.505	−1.951	−2.569
CNI	−1.619	1.619	1.619	−0.001	0.569	−0.064
C_2HI	−0.976	0.976	0.976	0.632	−0.067	−0.696
CH_2I_2	−6.072	46.324	0.471	−4.383	44.812	−1.192
HOI	−1.981	2.057	1.906	−0.357	1.003	0.219
C_3H_7I	0.653	−1.913	0.846	2.235	−2.926	−0.824
C_2H_5I	−0.509	2.886	−0.960	1.091	1.823	−2.600
CH_2ICl	−3.260	11.273	0.205	−1.616	10.124	−1.454
N_3I	−7.338	18.684	2.907	−5.629	17.458	1.203
I_2	−2.356	2.356	2.356	−0.726	1.298	0.661
C_2H_5OI	−1.195	4.680	−0.118	0.416	3.599	−1.772
C_2H_3I	−2.008	2.935	1.203	−0.384	1.871	−0.473
SiC_3H_9I	−1.604	1.605	1.602	0.014	0.556	−0.080
OI_2	−1.811	69.142	−5.613	−0.190	69.461	−7.176
			B2PLYP-D3(BJ,abc)-X2C			
0	−1.359	0.375	2.414	0.736	−1.152	0.239
2	−1.525	0.358	2.845	0.574	−1.169	0.660
3	−1.540	0.708	2.348	0.560	−0.824	0.174
4	−1.365	0.356	2.431	0.731	−1.171	0.256
23	−1.665	0.643	2.682	0.437	−0.888	0.501
24	−1.575	0.432	2.849	0.526	−1.096	0.664
25	−1.731	0.715	2.755	0.372	−0.817	0.572
26	−1.644	0.418	3.112	0.457	−1.109	0.922
34	−1.545	0.709	2.400	0.554	−0.823	0.225
35	−1.586	0.949	2.280	0.515	−0.587	0.108
234	−1.706	0.776	2.705	0.397	−0.757	0.524
235	−1.700	0.937	2.575	0.402	−0.599	0.397
236	−1.821	0.709	2.932	0.284	−0.823	0.746
245	−1.716	0.714	2.777	0.387	−0.818	0.594
246	−1.695	0.484	3.115	0.408	−1.044	0.925
345	−1.597	0.932	2.309	0.504	−0.603	0.136
2345	−1.758	1.002	2.606	0.346	−0.535	0.426
2346	−1.824	0.791	2.966	0.282	−0.742	0.779
2356	−1.783	0.996	2.723	0.322	−0.540	0.541
23456	−1.836	1.041	2.768	0.270	−0.496	0.585
IF	−3.810	3.810	3.810	−1.664	2.231	1.605
HI	−1.431	1.431	1.431	0.666	−0.112	−0.724
CH_3I	0.478	−0.478	−0.478	2.536	−1.992	−2.592
CNI	−2.133	2.133	2.133	−0.022	0.580	−0.036
C_2HI	−1.536	1.536	1.536	0.563	−0.009	−0.621
CH_2I_2	−6.543	46.975	0.918	−4.341	44.739	−1.226
HOI	−2.408	2.481	2.338	−0.291	0.922	0.164
C_3H_7I	0.159	−1.438	1.364	2.224	−2.938	−0.789
C_2H_5I	−0.997	3.404	−0.490	1.091	1.831	−2.604
CH_2ICl	−3.726	11.774	0.658	−1.581	10.074	−1.480
N_3I	−7.808	19.201	3.359	−5.579	17.388	1.163

I_2	−2.779	2.779	2.779	−0.654	1.215	0.595
C_2H_5OI	−1.687	5.235	0.350	0.416	3.634	−1.782
C_2H_3I	−2.524	3.473	1.699	−0.404	1.899	−0.461
SiC_3H_9I	−2.103	2.104	2.101	0.008	0.551	−0.068
OI_2	−2.481	68.635	−4.960	−0.362	69.112	−6.979
			B97-D3(BJ,abc)			
0	−52.125	48.546	55.961	−3.696	2.999	4.470
2	−50.232	46.452	54.510	−2.406	1.547	3.498
3	−51.296	47.450	55.035	−3.131	2.239	3.849
4	−51.896	48.100	55.904	−3.540	2.690	4.431
23	−49.399	45.051	53.730	−1.838	0.576	2.975
24	−50.125	46.236	54.462	−2.333	1.397	3.466
25	−49.711	45.830	53.624	−2.050	1.116	2.904
26	−48.608	44.887	53.062	−1.298	0.462	2.528
34	−50.963	46.944	55.071	−2.904	1.888	3.874
35	−50.341	46.680	54.331	−2.480	1.706	3.378
234	−49.131	44.838	53.751	−1.655	0.428	2.989
235	−48.546	44.648	53.013	−1.256	0.296	2.495
236	−48.042	43.713	52.368	−0.913	−0.352	2.063
245	−49.351	45.273	53.667	−1.805	0.730	2.933
246	−48.458	44.618	52.962	−1.196	0.275	2.461
345	−49.952	45.852	54.350	−2.215	1.131	3.390
2345	−48.239	43.904	53.102	−1.047	−0.220	2.555
2346	−47.660	43.415	52.357	−0.653	−0.559	2.056
2356	−46.957	42.896	51.813	−0.173	−0.918	1.691
23456	−46.632	42.162	51.873	0.048	−1.427	1.732
IF	−32.978	32.978	32.978	9.356	−7.796	−10.925
HI	−53.384	53.384	53.384	−4.554	6.354	2.744
CH_3I	−43.402	43.402	43.402	2.250	−0.567	−3.943
CNI	−44.407	44.407	44.407	1.565	0.129	−3.269
C_2HI	−54.001	54.001	54.001	−4.975	6.781	3.157
CH_2I_2	−50.134	102.142	42.898	−2.339	40.162	−4.281
HOI	−35.674	34.957	36.370	7.518	−6.423	−8.653
C_3H_7I	−49.843	45.633	54.856	−2.140	0.979	3.730
C_2H_5I	−49.434	54.094	46.555	−1.862	6.846	−1.831
CH_2ICl	−45.109	53.088	42.068	1.086	6.148	−4.837
N_3I	−44.093	57.822	38.731	1.779	9.431	−7.072
I_2	−32.527	32.527	32.527	9.663	−8.108	−11.228
C_2H_5OI	−46.164	49.892	44.759	0.367	3.932	−3.034
C_2H_3I	−51.101	54.684	47.988	−2.998	7.255	−0.871
SiC_3H_9I	−52.098	52.099	52.096	−3.677	5.463	1.881
OI_2	−81.291	−87.927	81.985	−23.577	−30.305	21.902
			B97-D3(BJ,abc)-DKH			
0	2.417	−1.013	−3.921	0.337	0.117	−0.628
2	2.604	−1.340	−4.033	0.528	−0.214	−0.743
3	2.640	−0.902	−4.330	0.565	0.229	−1.050
4	2.340	−1.170	−3.576	0.259	−0.042	−0.271
23	2.615	−0.947	−4.277	0.540	0.184	−0.995
24	2.555	−1.546	−3.681	0.478	−0.422	−0.379
25	2.938	−1.424	−4.464	0.869	−0.299	−1.189
26	2.733	−1.580	−4.113	0.660	−0.456	−0.825
34	2.612	−1.244	−4.010	0.536	−0.116	−0.719

35	2.796	−1.153	−4.586	0.724	−0.025	−1.315
234	2.704	−1.531	−3.967	0.631	−0.407	−0.674
235	2.946	−1.533	−4.565	0.877	−0.409	−1.293
236	2.834	−1.289	−4.379	0.763	−0.162	−1.100
245	2.893	−1.730	−4.125	0.824	−0.608	−0.838
246	2.689	−1.756	−3.784	0.615	−0.634	−0.486
345	2.852	−1.463	−4.343	0.782	−0.338	−1.063
2345	2.996	−1.856	−4.275	0.929	−0.736	−0.993
2346	2.866	−1.785	−4.062	0.796	−0.663	−0.773
2356	3.022	−1.777	−4.511	0.955	−0.656	−1.238
23456	3.028	−2.013	−4.218	0.961	−0.895	−0.934
IF	1.075	−1.075	−1.075	−1.034	0.055	2.317
HI	−0.487	0.487	0.487	−2.629	1.634	3.932
CH_3I	0.481	−0.480	−0.481	−1.641	0.656	2.931
CNI	4.957	−4.957	−4.957	2.932	−3.872	−1.699
C_2HI	3.520	−3.520	−3.520	1.464	−2.418	−0.212
CH_2I_2	−3.921	34.341	−0.312	−6.136	35.875	3.106
HOI	1.370	−1.383	−1.357	−0.732	−0.257	2.025
C_3H_7I	0.525	−1.724	0.903	−1.596	−0.602	4.363
C_2H_5I	−0.609	2.391	−0.492	−2.754	3.560	2.919
CH_2ICl	−0.487	4.531	−1.054	−2.629	5.724	2.338
N_3I	−3.247	15.253	−1.441	−5.448	16.569	1.938
I_2	0.045	−0.045	−0.045	−2.086	1.097	3.382
C_2H_5OI	1.419	−0.626	−1.718	−0.682	0.508	1.652
C_2H_3I	1.523	3.179	−5.610	−0.576	4.357	−2.374
SiC_3H_9I	−2.496	2.497	2.494	−4.680	3.667	6.008
OI_2	36.943	−66.119	−26.160	35.599	−68.016	−23.628
B97-D3(BJ,abc)-X2C						
0	1.929	−0.504	−3.456	0.314	0.144	−0.613
2	2.116	−0.834	−3.566	0.504	−0.189	−0.726
3	2.156	−0.397	−3.866	0.545	0.252	−1.035
4	1.852	−0.660	−3.111	0.236	−0.013	−0.257
23	2.134	−0.449	−3.812	0.522	0.200	−0.979
24	2.067	−1.038	−3.214	0.454	−0.394	−0.363
25	2.450	−0.914	−3.999	0.844	−0.269	−1.172
26	2.244	−1.076	−3.643	0.634	−0.431	−0.806
34	2.127	−0.739	−3.546	0.515	−0.092	−0.706
35	2.314	−0.655	−4.124	0.706	−0.007	−1.300
234	2.221	−1.030	−3.502	0.610	−0.386	−0.660
235	2.463	−1.034	−4.101	0.857	−0.390	−1.277
236	2.349	−0.785	−3.912	0.741	−0.139	−1.082
245	2.407	−1.222	−3.660	0.799	−0.579	−0.823
246	2.201	−1.251	−3.315	0.590	−0.608	−0.468
345	2.371	−0.964	−3.881	0.764	−0.319	−1.050
2345	2.514	−1.357	−3.811	0.908	−0.715	−0.979
2346	2.381	−1.283	−3.596	0.773	−0.640	−0.757
2356	2.539	−1.279	−4.047	0.934	−0.636	−1.221
23456	2.546	−1.515	−3.754	0.941	−0.874	−0.919
IF	0.691	−0.691	−0.691	−0.945	−0.044	2.234
HI	−1.027	1.027	1.027	−2.691	1.685	4.003
CH_3I	0.041	−0.041	−0.041	−1.605	0.611	2.903
CNI	4.479	−4.479	−4.479	2.906	−3.856	−1.666
C_2HI	2.989	−2.989	−2.989	1.391	−2.357	−0.132

CH_2I_2	−4.372	34.926	0.121	−6.091	35.804	3.069
HOI	0.966	−0.983	−0.949	−0.665	−0.338	1.968
C_3H_7I	0.043	−1.261	1.408	−1.603	−0.618	4.394
C_2H_5I	−1.086	2.895	−0.033	−2.750	3.565	2.911
CH_2ICl	−0.931	4.994	−0.618	−2.593	5.678	2.309
N_3I	−3.690	15.743	−1.017	−5.398	16.497	1.898
I_2	−0.359	0.359	0.359	−2.012	1.013	3.314
C_2H_5OI	0.949	−0.104	−1.268	−0.682	0.547	1.640
C_2H_3I	1.033	3.706	−5.151	−0.597	4.381	−2.357
SiC_3H_9I	−2.986	2.988	2.984	−4.682	3.659	6.017
OI_2	36.396	−67.276	−25.549	35.348	−68.366	−23.356
B97M-D3(BJ,abc)						
0	−49.005	44.213	54.140	−3.916	3.036	5.219
2	−46.893	41.725	52.741	−2.443	1.257	4.264
3	−48.251	43.117	53.243	−3.390	2.252	4.607
4	−48.760	43.811	53.986	−3.745	2.748	5.114
23	−46.145	40.364	51.904	−1.922	0.285	3.693
24	−46.784	41.551	52.621	−2.367	1.133	4.182
25	−46.397	40.952	51.888	−2.097	0.705	3.682
26	−45.025	39.776	51.310	−1.141	−0.135	3.287
34	−47.912	42.724	53.215	−3.154	1.971	4.588
35	−47.354	42.571	52.567	−2.764	1.862	4.146
234	−45.875	40.298	51.877	−1.733	0.238	3.674
235	−45.300	40.145	51.208	−1.332	0.129	3.218
236	−44.533	38.491	50.571	−0.797	−1.053	2.783
245	−46.055	40.558	51.874	−1.859	0.424	3.672
246	−44.905	39.571	51.163	−1.057	−0.281	3.187
345	−46.984	41.796	52.548	−2.506	1.309	4.132
2345	−45.025	39.464	51.265	−1.141	−0.358	3.256
2346	−44.164	38.412	50.528	−0.540	−1.109	2.754
2356	−43.474	38.057	49.952	−0.059	−1.363	2.360
23456	−43.176	37.354	50.002	0.149	−1.865	2.395
IF	−29.278	29.278	29.278	9.842	−7.636	−11.752
HI	−49.436	49.436	49.436	−4.216	6.767	2.008
CH_3I	−40.148	40.148	40.148	2.261	0.131	−4.332
CNI	−41.860	41.860	41.860	1.067	1.354	−3.164
C_2HI	−51.729	51.729	51.729	−5.816	8.406	3.574
CH_2I_2	−47.553	105.992	39.421	−2.903	47.174	−4.828
HOI	−31.863	31.316	32.395	8.039	−6.179	−9.624
C_3H_7I	−46.541	42.071	51.865	−2.198	1.505	3.666
C_2H_5I	−46.241	50.706	43.481	−1.988	7.674	−2.057
CH_2ICl	−43.424	54.437	39.226	−0.023	10.340	−4.962
N_3I	−40.508	53.120	35.582	2.010	9.399	−7.449
I_2	−26.806	26.806	26.806	11.566	−9.402	−13.440
C_2H_5OI	−44.839	50.087	42.862	−1.011	7.232	−2.479
C_2H_3I	−48.379	50.045	46.931	−3.479	7.202	0.298
SiC_3H_9I	−47.495	47.497	47.494	−2.863	5.381	0.683
OI_2	−79.041	−6.883	71.492	−24.863	23.635	17.064
B97M-D3(BJ,abc)-DKH						
0	3.314	−2.888	−3.771	0.071	0.285	−0.348
2	3.761	−3.613	−3.929	0.533	−0.463	−0.511
3	3.501	−2.793	−4.189	0.264	0.384	−0.780

4	3.271	−3.033	−3.523	0.027	0.136	−0.090
23	3.717	−3.191	−4.242	0.488	−0.027	−0.835
24	3.731	−3.805	−3.648	0.501	−0.661	−0.220
25	4.099	−3.839	−4.362	0.882	−0.696	−0.960
26	4.160	−4.230	−4.077	0.945	−1.100	−0.664
34	3.494	−3.064	−3.932	0.256	0.104	−0.515
35	3.634	−2.881	−4.455	0.402	0.293	−1.056
234	3.822	−3.679	−3.976	0.596	−0.531	−0.560
235	4.068	−3.653	−4.543	0.850	−0.504	−1.147
236	4.222	−4.043	−4.401	1.009	−0.907	−1.000
245	4.052	−4.029	−4.075	0.833	−0.893	−0.663
246	4.104	−4.370	−3.792	0.887	−1.245	−0.369
345	3.688	−3.165	−4.249	0.457	−0.001	−0.842
2345	4.101	−3.942	−4.280	0.884	−0.803	−0.875
2346	4.248	−4.373	−4.109	1.036	−1.248	−0.697
2356	4.400	−4.232	−4.602	1.194	−1.102	−1.209
23456	4.392	−4.456	−4.316	1.185	−1.334	−0.912
IF	3.090	−3.090	−3.090	−0.160	0.077	0.357
HI	1.223	−1.223	−1.223	−2.091	2.005	2.291
CH_3I	1.486	−1.486	−1.487	−1.818	1.733	2.018
CNI	5.811	−5.811	−5.811	2.652	−2.733	−2.461
C_2HI	4.120	−4.120	−4.120	0.904	−0.986	−0.709
CH_2I_2	−3.426	40.168	−1.686	−6.895	44.748	1.812
HOI	3.290	−3.170	−3.406	0.046	−0.005	0.030
C_3H_7I	1.360	−2.819	0.378	−1.949	0.356	3.949
C_2H_5I	0.210	1.435	−1.226	−3.138	4.750	2.287
CH_2ICl	−0.897	7.537	−1.634	−4.282	11.052	1.865
N_3I	−1.675	12.781	−2.663	−5.085	16.467	0.800
I_2	3.616	−3.616	−3.616	0.383	−0.467	−0.188
C_2H_5OI	0.531	1.490	−1.292	−2.806	4.807	2.219
C_2H_3I	2.152	1.093	−4.971	−1.130	4.397	−1.591
SiC_3H_9I	−0.941	0.942	0.939	−4.327	4.241	4.530
OI_2	3.270	−9.553	−1.929	0.026	−13.133	1.560
B97M-D3(BJ,abc)-X2C						
0	2.816	−2.372	−3.292	0.048	0.314	−0.336
2	3.264	−3.102	−3.448	0.509	−0.436	−0.496
3	3.006	−2.281	−3.711	0.244	0.408	−0.768
4	2.772	−2.516	−3.043	0.004	0.166	−0.079
23	3.226	−2.687	−3.763	0.470	−0.009	−0.822
24	3.233	−3.293	−3.166	0.477	−0.632	−0.206
25	3.602	−3.324	−3.883	0.857	−0.664	−0.945
26	3.664	−3.722	−3.594	0.920	−1.073	−0.647
34	2.998	−2.552	−3.455	0.236	0.129	−0.504
35	3.142	−2.375	−3.979	0.384	0.311	−1.044
234	3.329	−3.173	−3.497	0.576	−0.509	−0.547
235	3.576	−3.149	−4.066	0.830	−0.484	−1.133
236	3.729	−3.536	−3.922	0.987	−0.882	−0.985
245	3.555	−3.517	−3.597	0.809	−0.862	−0.650
246	3.608	−3.862	−3.309	0.863	−1.217	−0.354
345	3.197	−2.659	−3.773	0.440	0.019	−0.831
2345	3.610	−3.438	−3.803	0.865	−0.781	−0.863
2346	3.755	−3.868	−3.629	1.014	−1.223	−0.684
2356	3.910	−3.730	−4.125	1.173	−1.081	−1.194

23456	3.901	−3.955	−3.839	1.165	−1.312	−0.900
IF	2.704	−2.704	−2.704	−0.067	−0.027	0.270
HI	0.674	−0.674	−0.674	−2.155	2.059	2.362
CH_3I	1.037	−1.037	−1.037	−1.781	1.686	1.988
CNI	5.323	−5.323	−5.323	2.627	−2.718	−2.429
C_2HI	3.578	−3.578	−3.578	0.832	−0.925	−0.630
CH_2I_2	−3.889	40.797	−1.246	−6.848	44.671	1.773
HOI	2.882	−2.766	−2.995	0.116	−0.090	−0.030
C_3H_7I	0.867	−2.347	0.896	−1.956	0.340	3.980
C_2H_5I	−0.278	1.950	−0.756	−3.134	4.756	2.278
CH_2ICl	−1.356	8.027	−1.187	−4.242	11.000	1.833
N_3I	−2.124	13.276	−2.231	−5.032	16.392	0.757
I_2	3.216	−3.216	−3.216	0.459	−0.552	−0.257
C_2H_5OI	0.043	2.036	−0.826	−2.804	4.843	2.205
C_2H_3I	1.650	1.626	−4.496	−1.151	4.422	−1.577
SiC_3H_9I	−1.441	1.442	1.439	−4.329	4.233	4.540
OI_2	2.611	−10.298	−1.260	−0.162	−13.333	1.758
			BP86-D3(BJ,abc)			
0	−51.083	47.314	55.123	−3.855	3.217	4.635
2	−49.080	45.005	53.693	−2.478	1.599	3.670
3	−50.219	46.170	54.155	−3.261	2.416	3.982
4	−50.863	46.819	55.133	−3.703	2.870	4.642
23	−48.300	43.662	52.920	−1.942	0.659	3.149
24	−48.964	44.696	53.723	−2.398	1.383	3.691
25	−48.438	44.145	52.767	−2.037	0.997	3.046
26	−47.339	43.177	52.322	−1.281	0.319	2.745
34	−49.878	45.595	54.255	−3.026	2.013	4.050
35	−49.228	45.377	53.427	−2.580	1.860	3.491
234	−47.967	43.279	53.011	−1.713	0.390	3.211
235	−47.315	43.072	52.178	−1.265	0.245	2.649
236	−46.770	41.897	51.638	−0.890	−0.578	2.284
245	−48.097	43.571	52.887	−1.802	0.595	3.127
246	−47.196	42.846	52.299	−1.183	0.087	2.730
345	−48.825	44.460	53.506	−2.302	1.218	3.544
2345	−46.987	42.216	52.340	−1.039	−0.355	2.758
2346	−46.366	41.546	51.697	−0.612	−0.824	2.324
2356	−45.631	41.053	51.105	−0.107	−1.169	1.925
23456	−45.305	40.247	51.237	0.117	−1.734	2.013
IF	−31.401	31.401	31.401	9.675	−7.933	−11.367
HI	−51.196	51.196	51.196	−3.933	5.937	1.986
CH_3I	−42.872	42.872	42.872	1.789	0.105	−3.629
CNI	−43.237	43.237	43.237	1.539	0.361	−3.383
C_2HI	−52.832	52.832	52.832	−5.057	7.084	3.090
CH_2I_2	−49.183	98.808	42.278	−2.549	39.297	−4.029
HOI	−34.271	33.457	35.062	7.702	−6.492	−8.897
C_3H_7I	−48.982	44.773	53.993	−2.410	1.437	3.873
C_2H_5I	−48.667	52.937	46.028	−2.194	7.157	−1.500
CH_2ICl	−43.900	50.556	41.363	1.083	5.489	−4.647
N_3I	−42.792	55.616	37.784	1.844	9.034	−7.061
I_2	−31.411	31.411	31.411	9.668	−7.925	−11.359
C_2H_5OI	−45.022	47.654	44.030	0.312	3.455	−2.848
C_2H_3I	−49.786	53.491	46.566	−2.963	7.546	−1.137
SiC_3H_9I	−51.716	51.718	51.714	−4.290	6.303	2.336

OI_2	−78.731	−75.040	78.344	−22.860	−22.644	20.298
BP86-D3(BJ,abc)-DKH						
0	3.094	−1.844	−4.433	0.288	0.364	−1.232
2	3.381	−2.353	−4.543	0.583	−0.157	−1.345
3	3.351	−1.776	−4.882	0.553	0.433	−1.696
4	3.012	−2.043	−4.035	0.204	0.160	−0.820
23	3.350	−1.909	−4.786	0.552	0.297	−1.597
24	3.342	−2.636	−4.130	0.544	−0.446	−0.918
25	3.820	−2.638	−5.012	1.036	−0.449	−1.830
26	3.614	−2.812	−4.575	0.824	−0.626	−1.378
34	3.332	−2.176	−4.513	0.533	0.024	−1.314
35	3.543	−2.053	−5.167	0.750	0.150	−1.991
234	3.497	−2.637	−4.422	0.702	−0.447	−1.220
235	3.798	−2.659	−5.102	1.012	−0.470	−1.924
236	3.728	−2.614	−4.841	0.941	−0.424	−1.654
245	3.764	−2.960	−4.614	0.977	−0.778	−1.419
246	3.566	−3.039	−4.185	0.774	−0.858	−0.976
345	3.614	−2.437	−4.876	0.823	−0.242	−1.690
2345	3.867	−3.075	−4.756	1.083	−0.895	−1.565
2346	3.775	−3.149	−4.467	0.989	−0.970	−1.267
2356	3.958	−3.121	−4.959	1.177	−0.942	−1.775
23456	3.967	−3.418	−4.610	1.186	−1.246	−1.415
IF	2.293	−2.293	−2.293	−0.536	−0.095	0.980
HI	1.166	−1.166	−1.166	−1.695	1.057	2.145
CH_3I	0.731	−0.731	−0.732	−2.143	1.501	2.594
CNI	5.834	−5.834	−5.834	3.108	−3.716	−2.680
C_2HI	4.375	−4.375	−4.375	1.606	−2.224	−1.172
CH_2I_2	−3.275	31.553	−0.660	−6.265	34.512	2.668
HOI	2.408	−2.503	−2.315	−0.418	−0.310	0.957
C_3H_7I	0.994	−2.200	0.442	−1.873	0.000	3.806
C_2H_5I	−0.197	1.670	−0.714	−3.098	3.957	2.612
CH_2ICl	0.315	2.679	−1.456	−2.571	4.989	1.845
N_3I	−2.316	13.582	−2.084	−5.279	16.137	1.196
I_2	0.821	−0.821	−0.821	−2.051	1.410	2.501
C_2H_5OI	2.086	−2.151	−2.061	−0.749	0.050	1.220
C_2H_3I	2.433	2.379	−6.614	−0.392	4.682	−3.486
SiC_3H_9I	−2.561	2.563	2.559	−5.531	4.869	5.995
OI_2	4.630	−65.831	2.742	1.869	−69.561	6.183
BP86-D3(BJ,abc)-X2C						
0	2.608	−1.338	−3.970	0.265	0.391	−1.220
2	2.896	−1.851	−4.078	0.560	−0.131	−1.331
3	2.869	−1.274	−4.421	0.533	0.456	−1.684
4	2.526	−1.536	−3.571	0.181	0.189	−0.809
23	2.871	−1.414	−4.323	0.535	0.314	−1.583
24	2.856	−2.132	−3.664	0.520	−0.418	−0.905
25	3.337	−2.133	−4.550	1.011	−0.419	−1.816
26	3.129	−2.312	−4.108	0.799	−0.600	−1.362
34	2.850	−1.674	−4.051	0.513	0.049	−1.303
35	3.064	−1.557	−4.707	0.733	0.168	−1.978
234	3.016	−2.140	−3.958	0.683	−0.425	−1.208
235	3.319	−2.165	−4.641	0.993	−0.451	−1.910
236	3.247	−2.116	−4.377	0.919	−0.400	−1.638

245	3.280	−2.457	−4.151	0.954	−0.748	−1.406
246	3.081	−2.539	−3.718	0.750	−0.831	−0.961
345	3.136	−1.941	−4.416	0.805	−0.223	−1.679
2345	3.388	−2.580	−4.294	1.064	−0.873	−1.553
2346	3.293	−2.651	−4.003	0.967	−0.946	−1.253
2356	3.479	−2.628	−4.496	1.157	−0.922	−1.761
23456	3.488	−2.925	−4.148	1.166	−1.224	−1.403
IF	1.914	−1.914	−1.914	−0.446	−0.195	0.895
HI	0.632	−0.632	−0.632	−1.759	1.110	2.214
CH_3I	0.293	−0.292	−0.293	−2.106	1.455	2.563
CNI	5.359	−5.359	−5.359	3.082	−3.700	−2.648
C_2HI	3.847	−3.847	−3.847	1.534	−2.162	−1.093
CH_2I_2	−3.724	32.127	−0.228	−6.219	34.442	2.630
HOI	2.008	−2.107	−1.911	−0.350	−0.391	0.898
C_3H_7I	0.514	−1.738	0.945	−1.879	−0.017	3.836
C_2H_5I	−0.672	2.172	−0.255	−3.093	3.962	2.601
CH_2ICl	−0.126	3.136	−1.022	−2.534	4.943	1.813
N_3I	−2.755	14.067	−1.662	−5.227	16.065	1.154
I_2	0.420	−0.420	−0.420	−1.975	1.325	2.432
C_2H_5OI	1.618	−1.634	−1.612	−0.749	0.090	1.206
C_2H_3I	1.945	2.903	−6.159	−0.413	4.706	−3.471
SiC_3H_9I	−3.052	3.054	3.050	−5.531	4.859	6.001
OI_2	3.991	−66.786	3.414	1.682	−69.709	6.376

Tab. S20: The relative deviations (RD) of the quantum chemical calculation results from the experimental results for the diagonal components of the nuclear quadrupole coupling tensor in the nuclear principal axis system. The left column shows the raw results, whereas results in the right column were obtained by applying semi-experimental scaling. The individual RDs, RD(χ_{xx}), RD(χ_{yy}) and RD(χ_{zz}) are defined according to Eq. 6 of the main text. Values are tabulated for the fluoroiodobenzenes, iodobenzene, as well as for the molecules in Bailey's[8] original training set. All geometries were optimised at the B3LYP-D3(BJ,abc)/ma-def2-TZVP level of theory. The nomenclature for the fluoroiodobenzenes and iodobenzene is shown in Fig. 1 of the main text. Functionals are combined with the x2c-TZVPPall basis set, unless otherwise stated. In some cases, the basis set was decontracted. This is indicated by "d.". Additionally, "Bailey" describes the level of theory proposed by Bailey, as described in Sec. 2.3 of the main text, utilising the respective optimised nuclear quadrupole moments Q_{eff}. This level of theory has a self-referencing problem due to the inclusion of its training set into the testing set, as discussed in the main text. Details of the remaining functionals used are given in Sec. 2.3 of the main text. All values are given in percent.

Molecule	RD(χ_{xx})	RD(χ_{yy})	RD(χ_{zz})	RD(χ_{xx})	RD(χ_{yy})	RD(χ_{zz})
			PBE/def2-SVP			
0	−98.250	−98.224	98.236	−1.067	0.025	0.457
2	−98.237	−98.237	98.237	−0.345	−0.715	0.493
3	−98.257	−98.224	98.239	−1.445	0.048	0.623
23	−98.239	−98.239	98.239	−0.436	−0.799	0.580
24	−98.229	−98.240	98.235	0.128	−0.898	0.366
25	−98.243	−98.236	98.239	−0.693	−0.651	0.620
26	−98.220	−98.249	98.236	0.603	−1.392	0.431
34	−98.250	−98.228	98.239	−1.104	−0.177	0.581
35	−98.260	−98.224	98.241	−1.666	0.040	0.729
234	−98.232	−98.244	98.238	−0.042	−1.089	0.547
235	−98.243	−98.238	98.240	−0.658	−0.746	0.655

236	−98.222	−98.250	98.237	0.519	−1.433	0.492
245	−98.236	−98.241	98.238	−0.265	−0.921	0.564
246	−98.211	−98.252	98.234	1.100	−1.572	0.292
345	−98.256	−98.230	98.242	−1.433	−0.283	0.793
2356	−98.221	−98.251	98.238	0.544	−1.508	0.521
23456	−98.214	−98.256	98.237	0.940	−1.767	0.471
2345	−98.237	−98.244	98.240	−0.319	−1.079	0.673
2346	−98.214	−98.255	98.236	0.967	−1.713	0.429
4	−98.243	−98.226	98.234	−0.684	−0.107	0.344
IF	−98.236	−98.236	98.236	−0.265	−0.628	0.409
HI	−98.234	−98.234	98.234	−0.153	−0.517	0.297
CH_3I	−98.179	−98.178	98.178	2.965	2.591	−2.817
CNI	−98.270	−98.270	98.270	−2.199	−2.555	2.340
C_2HI	−98.294	−98.294	98.294	−3.563	−3.914	3.701
CH_2I_2	−98.246	−98.142	98.193	−0.846	4.632	−1.998
HOI	−98.265	−98.217	98.241	−1.951	0.395	0.722
C_3H_7I	−98.172	−98.197	98.185	3.311	1.540	−2.453
C_2H_5I	−98.191	−98.169	98.180	2.254	3.117	−2.729
CH_2ICl	−98.244	−98.171	98.207	−0.753	2.985	−1.218
N_3I	−98.160	−98.161	98.161	4.001	3.573	−3.826
I_2	−98.166	−98.166	98.166	3.688	3.311	−3.539
C_2H_5OI	−98.267	−98.204	98.234	−2.055	1.169	0.300
C_2H_3I	−98.292	−98.213	98.250	−3.438	0.655	1.230
SiC_3H_9I	−98.138	−98.138	98.138	5.269	4.892	−5.121
OI_2	99.375	98.198	−98.321	64.667	−1.516	−5.213
			B3LYP-D3(BJ,abc)/d.			
0	−11.854	−10.680	11.247	−0.491	−0.160	0.292
2	−12.028	−10.890	11.423	−0.688	−0.395	0.490
3	−12.144	−10.606	11.345	−0.819	−0.078	0.403
23	−12.264	−10.843	11.507	−0.954	−0.342	0.585
24	−11.871	−10.958	11.390	−0.510	−0.471	0.453
25	−12.332	−10.800	11.515	−1.031	−0.294	0.593
26	−12.248	−11.025	11.582	−0.936	−0.545	0.668
34	−11.997	−10.713	11.335	−0.653	−0.197	0.392
35	−12.381	−10.549	11.426	−1.086	−0.014	0.493
234	−12.105	−10.948	11.495	−0.775	−0.459	0.571
235	−12.524	−10.765	11.585	−1.247	−0.255	0.672
236	−12.490	−10.945	11.648	−1.209	−0.456	0.743
245	−12.165	−10.900	11.496	−0.842	−0.406	0.572
246	−12.074	−11.093	11.544	−0.739	−0.622	0.627
345	−12.263	−10.704	11.456	−0.953	−0.187	0.528
2356	−12.694	−10.919	11.727	−1.440	−0.427	0.832
23456	−12.499	−11.020	11.701	−1.219	−0.540	0.803
2345	−12.358	−10.887	11.580	−1.060	−0.391	0.666
2346	−12.300	−11.070	11.636	−0.995	−0.596	0.730
4	−11.721	−10.769	11.232	−0.341	−0.260	0.276
IF	−9.012	−9.012	9.012	2.717	1.704	−2.218
HI	−10.673	−10.673	10.673	0.842	−0.152	−0.353
CH_3I	−10.612	−10.612	10.612	0.911	−0.084	−0.421
CNI	−12.650	−12.650	12.650	−1.390	−2.362	1.868
C_2HI	−12.604	−12.604	12.604	−1.338	−2.310	1.817
CH_2I_2	−11.218	−10.144	10.672	0.226	0.439	−0.354
HOI	−10.088	−9.741	9.912	1.503	0.890	−1.207

C_3H_7I	−10.646	−11.220	10.937	0.873	−0.764	−0.055
C_2H_5I	−11.008	−10.486	10.746	0.464	0.056	−0.270
CH_2ICl	−11.599	−10.310	10.936	−0.203	0.253	−0.057
N_3I	−8.926	−8.327	8.626	2.815	2.470	−2.652
I_2	−9.884	−9.884	9.884	1.733	0.730	−1.239
C_2H_5OI	−12.786	−11.884	12.309	−1.543	−1.506	1.486
C_2H_3I	−13.014	−9.855	11.350	−1.801	0.762	0.408
SiC_3H_9I	−9.011	−9.004	9.008	2.719	1.713	−2.223
OI_2	24.801	8.521	−10.225	15.107	−2.253	0.856
B3LYP-D3(BJ,abc)-DKH2/d.						
0	−0.070	0.236	−0.088	0.025	0.031	−0.015
2	−0.079	−0.105	0.093	0.016	−0.309	0.166
3	−0.398	0.287	0.042	−0.303	0.082	0.116
23	−0.351	−0.083	0.208	−0.256	−0.287	0.281
24	0.065	−0.176	0.062	0.160	−0.379	0.135
25	−0.422	−0.038	0.217	−0.327	−0.242	0.290
26	−0.142	−0.338	0.249	−0.046	−0.541	0.322
34	−0.250	0.159	0.039	−0.155	−0.046	0.113
35	−0.664	0.318	0.152	−0.570	0.113	0.225
234	−0.214	−0.200	0.206	−0.118	−0.403	0.279
235	−0.642	−0.029	0.315	−0.547	−0.233	0.388
236	−0.424	−0.279	0.345	−0.329	−0.483	0.418
245	−0.268	−0.151	0.206	−0.173	−0.355	0.279
246	0.002	−0.409	0.220	0.098	−0.612	0.293
345	−0.556	0.128	0.202	−0.461	−0.077	0.275
2356	−0.662	−0.280	0.454	−0.567	−0.483	0.527
23456	−0.501	−0.401	0.447	−0.406	−0.604	0.520
2345	−0.500	−0.172	0.326	−0.405	−0.376	0.399
2346	−0.266	−0.418	0.348	−0.171	−0.622	0.422
4	0.066	0.136	−0.102	0.162	−0.068	−0.029
IF	0.919	0.919	−0.919	1.016	0.713	−0.845
HI	1.261	1.261	−1.261	1.357	1.054	−1.186
CH_3I	0.617	0.617	−0.617	0.713	0.412	−0.543
CNI	−1.312	−1.312	1.312	−1.218	−1.514	1.385
C_2HI	−0.909	−0.909	0.909	−0.814	−1.111	0.981
CH_2I_2	−1.633	0.925	0.329	−1.539	0.719	0.402
HOI	−0.056	0.428	−0.189	0.040	0.223	−0.115
C_3H_7I	0.527	−0.396	−0.059	0.623	−0.599	0.015
C_2H_5I	−0.003	0.722	−0.361	0.092	0.516	−0.287
CH_2ICl	−0.987	0.620	0.160	−0.892	0.414	0.234
N_3I	1.401	1.855	−1.628	1.497	1.647	−1.553
I_2	1.097	1.097	−1.097	1.193	0.890	−1.023
C_2H_5OI	−2.209	−0.991	1.565	−2.116	−1.193	1.637
C_2H_3I	−1.611	1.333	0.060	−1.517	1.126	0.133
SiC_3H_9I	3.845	3.851	−3.848	3.944	3.639	−3.772
OI_2	−28.430	−0.686	3.588	−28.553	−0.480	3.512
B3LYP-D3(BJ,abc)-X2C/d.						
0	0.413	0.754	−0.590	0.042	0.061	−0.038
2	0.407	0.411	−0.409	0.035	−0.281	0.141
3	0.084	0.801	−0.456	−0.286	0.107	0.094
23	0.133	0.430	−0.291	−0.237	−0.262	0.258
24	0.551	0.341	−0.440	0.178	−0.350	0.110

25	0.063	0.475	−0.283	−0.308	−0.217	0.267
26	0.347	0.176	−0.253	−0.025	−0.514	0.296
34	0.232	0.674	−0.459	−0.139	−0.020	0.091
35	−0.183	0.827	−0.344	−0.553	0.133	0.206
234	0.270	0.314	−0.293	−0.101	−0.377	0.257
235	−0.160	0.480	−0.182	−0.529	−0.212	0.367
236	0.062	0.232	−0.155	−0.309	−0.458	0.394
245	0.216	0.363	−0.293	−0.155	−0.329	0.256
246	0.490	0.105	−0.282	0.118	−0.584	0.267
345	−0.075	0.637	−0.293	−0.445	−0.056	0.256
2356	−0.178	0.228	−0.043	−0.548	−0.462	0.505
23456	−0.018	0.108	−0.050	−0.388	−0.582	0.499
2345	−0.018	0.337	−0.170	−0.388	−0.354	0.379
2346	0.218	0.093	−0.151	−0.153	−0.596	0.398
4	0.550	0.656	−0.604	0.178	−0.038	−0.053
IF	1.314	1.314	−1.314	0.939	0.617	−0.759
HI	1.809	1.809	−1.809	1.432	1.108	−1.251
CH_3I	1.065	1.066	−1.066	0.691	0.370	−0.512
CNI	−0.816	−0.816	0.816	−1.183	−1.499	1.360
C_2HI	−0.363	−0.363	0.363	−0.732	−1.050	0.910
CH_2I_2	−1.195	1.366	−0.111	−1.561	0.668	0.438
HOI	0.353	0.846	−0.603	−0.019	0.152	−0.051
C_3H_7I	1.010	0.077	−0.536	0.636	−0.613	0.015
C_2H_5I	0.453	1.190	−0.824	0.081	0.494	−0.271
CH_2ICl	−0.542	1.066	−0.285	−0.911	0.370	0.265
N_3I	1.839	2.282	−2.061	1.463	1.578	−1.502
I_2	1.508	1.508	−1.508	1.132	0.809	−0.952
C_2H_5OI	−1.751	−0.537	1.109	−2.115	−1.222	1.652
C_2H_3I	−1.133	1.843	−0.435	−1.499	1.142	0.115
SiC_3H_9I	4.345	4.352	−4.348	3.959	3.633	−3.776
OI_2	−29.279	−1.346	4.269	−28.801	−0.648	3.697
			Bailey			
0	−4.156	0.262	1.870	−1.245	0.575	0.293
2	−4.487	0.121	2.036	−1.586	0.433	0.461
3	−4.405	0.223	2.001	−1.502	0.535	0.426
23	−4.590	−0.029	2.163	−1.692	0.282	0.590
24	−4.113	0.034	1.926	−1.200	0.346	0.350
25	−4.752	0.094	2.166	−1.859	0.406	0.593
26	−4.759	−0.046	2.191	−1.867	0.265	0.619
34	−4.146	0.095	1.960	−1.235	0.407	0.384
35	−4.525	0.194	2.064	−1.625	0.506	0.489
234	−4.282	−0.226	2.144	−1.375	0.085	0.570
235	−4.733	−0.032	2.222	−1.840	0.280	0.651
236	−4.861	−0.177	2.310	−1.971	0.134	0.740
245	−4.432	−0.068	2.124	−1.530	0.244	0.550
246	−4.372	−0.148	2.092	−1.468	0.163	0.518
345	−4.366	−0.034	2.124	−1.461	0.277	0.551
2356	−4.850	−0.317	2.381	−1.960	−0.007	0.812
23456	−4.564	−0.498	2.370	−1.666	−0.188	0.800
2345	−4.479	−0.273	2.254	−1.578	0.038	0.683
2346	−4.525	−0.371	2.284	−1.625	−0.061	0.713
4	−3.835	0.230	1.747	−0.914	0.542	0.168
IF	−1.636	−1.636	1.636	1.352	−1.329	0.055

HI	1.389	1.389	−1.389	4.469	1.705	−3.019
CH_3I	0.459	0.459	−0.459	3.510	0.772	−2.074
CNI	−4.129	−4.129	4.129	−1.217	−3.830	2.587
C_2HI	−3.668	−3.668	3.668	−0.743	−3.368	2.120
CH_2I_2	−1.205	1.024	0.069	1.795	1.338	−1.537
HOI	−2.762	−1.999	2.376	0.191	−1.693	0.806
C_3H_7I	0.100	0.041	−0.070	3.141	0.353	−1.679
C_2H_5I	0.062	0.353	−0.208	3.101	0.666	−1.819
CH_2ICl	−1.246	1.396	−0.113	1.753	1.712	−1.723
N_3I	−0.466	1.277	−0.406	2.558	1.592	−2.020
I_2	1.047	1.047	−1.047	4.116	1.362	−2.671
C_2H_5OI	−4.791	−3.128	3.912	−1.899	−2.826	2.367
C_2H_3I	−5.486	0.839	2.154	−2.615	1.153	0.581
SiC_3H_9I	4.113	4.120	−4.117	7.275	4.445	−5.791
OI_2	−47.757	0.706	4.365	−52.244	0.396	6.042
			B3LYP-D3(BJ,abc)			
0	60.300	49.604	−54.767	6.213	2.216	−4.356
2	58.976	47.637	−52.944	5.336	0.872	−3.127
3	59.472	48.800	−53.929	5.665	1.667	−3.791
23	58.159	46.805	−52.116	4.794	0.303	−2.568
24	58.675	47.452	−52.758	5.136	0.746	−3.001
25	58.195	46.908	−52.171	4.818	0.374	−2.606
26	57.548	45.963	−51.236	4.390	−0.272	−1.975
34	57.812	49.731	−53.646	4.565	2.302	−3.600
35	58.758	48.021	−53.158	5.191	1.134	−3.271
234	57.966	46.469	−51.905	4.667	0.074	−2.426
235	57.437	46.023	−51.342	4.316	−0.231	−2.046
236	56.830	45.243	−50.521	3.914	−0.764	−1.492
245	58.010	46.556	−51.952	4.696	0.133	−2.458
246	57.218	45.825	−51.068	4.171	−0.367	−1.861
345	58.025	47.889	−52.780	4.705	1.044	−3.016
2356	56.139	44.288	−49.684	3.456	−1.417	−0.929
23456	56.032	43.696	−49.374	3.385	−1.821	−0.719
2345	57.342	45.457	−51.054	4.253	−0.618	−1.852
2346	56.617	44.882	−50.285	3.773	−1.011	−1.333
4	57.587	51.512	−54.466	4.415	3.519	−4.153
IF	35.082	35.082	−35.082	−10.496	−7.707	8.918
HI	53.967	53.967	−53.967	2.017	5.197	−3.817
CH_3I	44.290	44.291	−44.291	−4.395	−1.415	2.708
CNI	48.493	48.493	−48.493	−1.610	1.456	−0.125
C_2HI	56.873	56.873	−56.873	3.943	7.182	−5.776
CH_2I_2	44.480	43.986	−44.225	−4.269	−1.623	2.753
HOI	36.146	38.180	−37.175	−9.791	−5.590	7.506
C_3H_7I	50.571	46.750	−48.631	−0.234	0.265	−0.218
C_2H_5I	44.941	47.552	−46.254	−3.964	0.813	1.384
CH_2ICl	42.963	43.633	−43.308	−5.274	−1.864	3.371
N_3I	39.327	41.587	−40.458	−7.684	−3.262	5.293
I_2	33.408	33.408	−33.408	−11.605	−8.850	10.046
C_2H_5OI	41.679	43.379	−42.577	−6.125	−2.038	3.864
C_2H_3I	52.563	50.358	−51.402	1.087	2.730	−2.087
SiC_3H_9I	52.943	52.950	−52.947	1.338	4.502	−3.128
OI_2	−27.785	−85.430	79.398	15.331	−26.693	20.964

B3LYP-D3(BJ,abc)-DKH						
0	−0.070	0.236	−0.088	0.025	0.031	−0.015
2	−0.079	−0.105	0.093	0.016	−0.309	0.166
3	−0.398	0.287	0.042	−0.303	0.082	0.116
23	−0.351	−0.083	0.208	−0.256	−0.287	0.281
24	0.065	−0.176	0.062	0.160	−0.379	0.135
25	−0.422	−0.038	0.217	−0.327	−0.242	0.290
26	−0.142	−0.338	0.249	−0.046	−0.541	0.322
34	−0.250	0.159	0.039	−0.155	−0.046	0.113
35	−0.664	0.318	0.152	−0.570	0.113	0.225
234	−0.214	−0.200	0.206	−0.118	−0.403	0.279
235	−0.642	−0.029	0.315	−0.547	−0.233	0.388
236	−0.424	−0.279	0.345	−0.329	−0.483	0.418
245	−0.268	−0.151	0.206	−0.173	−0.355	0.279
246	0.002	−0.409	0.220	0.098	−0.612	0.293
345	−0.556	0.128	0.202	−0.461	−0.077	0.275
2356	−0.662	−0.280	0.454	−0.567	−0.483	0.527
23456	−0.501	−0.401	0.447	−0.406	−0.604	0.520
2345	−0.500	−0.172	0.326	−0.405	−0.376	0.399
2346	−0.266	−0.418	0.348	−0.171	−0.622	0.422
4	0.066	0.136	−0.102	0.162	−0.068	−0.029
IF	0.919	0.919	−0.919	1.016	0.713	−0.845
HI	1.261	1.261	−1.261	1.357	1.054	−1.186
CH_3I	0.617	0.617	−0.617	0.713	0.412	−0.543
CNI	−1.312	−1.312	1.312	−1.218	−1.514	1.385
C_2HI	−0.909	−0.909	0.909	−0.814	−1.111	0.981
CH_2I_2	−1.633	0.925	0.329	−1.539	0.719	0.402
HOI	−0.056	0.428	−0.189	0.040	0.223	−0.115
C_3H_7I	0.527	−0.396	−0.059	0.623	−0.599	0.015
C_2H_5I	−0.003	0.722	−0.361	0.092	0.516	−0.287
CH_2ICl	−0.987	0.620	0.160	−0.892	0.414	0.234
N_3I	1.401	1.855	−1.628	1.497	1.647	−1.553
I_2	1.097	1.097	−1.097	1.193	0.890	−1.023
C_2H_5OI	−2.209	−0.991	1.565	−2.116	−1.193	1.637
C_2H_3I	−1.611	1.333	0.060	−1.517	1.126	0.133
SiC_3H_9I	3.845	3.851	−3.848	3.944	3.639	−3.772
OI_2	−28.430	−0.686	3.588	−28.553	−0.480	3.512
B3LYP-D3(BJ,abc)-X2C						
0	0.413	0.754	−0.590	0.042	0.061	−0.038
2	0.407	0.411	−0.409	0.035	−0.281	0.141
3	0.084	0.801	−0.456	−0.286	0.107	0.094
23	0.133	0.430	−0.291	−0.237	−0.262	0.258
24	0.551	0.341	−0.440	0.178	−0.350	0.110
25	0.063	0.475	−0.283	−0.308	−0.217	0.267
26	0.347	0.176	−0.253	−0.025	−0.514	0.296
34	0.232	0.674	−0.459	−0.139	−0.020	0.091
35	−0.183	0.827	−0.344	−0.553	0.133	0.206
234	0.270	0.314	−0.293	−0.101	−0.377	0.257
235	−0.160	0.480	−0.182	−0.529	−0.212	0.367
236	0.062	0.232	−0.155	−0.309	−0.458	0.394
245	0.216	0.363	−0.293	−0.155	−0.329	0.256
246	0.490	0.105	−0.282	0.118	−0.584	0.267
345	−0.075	0.637	−0.293	−0.445	−0.056	0.256

2356	−0.178	0.228	−0.043	−0.548	−0.462	0.505
23456	−0.018	0.108	−0.050	−0.388	−0.582	0.499
2345	−0.018	0.337	−0.170	−0.388	−0.354	0.379
2346	0.218	0.093	−0.151	−0.153	−0.596	0.398
4	0.550	0.656	−0.604	0.178	−0.038	−0.053
IF	1.314	1.314	−1.314	0.939	0.617	−0.759
HI	1.809	1.809	−1.809	1.432	1.108	−1.251
CH_3I	1.065	1.066	−1.066	0.691	0.370	−0.512
CNI	−0.816	−0.816	0.816	−1.183	−1.499	1.360
C_2HI	−0.363	−0.363	0.363	−0.732	−1.050	0.910
CH_2I_2	−1.195	1.366	−0.111	−1.561	0.668	0.438
HOI	0.353	0.846	−0.603	−0.019	0.152	−0.051
C_3H_7I	1.010	0.077	−0.536	0.636	−0.613	0.015
C_2H_5I	0.453	1.190	−0.824	0.081	0.494	−0.271
CH_2ICl	−0.542	1.066	−0.285	−0.911	0.370	0.265
N_3I	1.839	2.282	−2.061	1.463	1.578	−1.502
I_2	1.508	1.508	−1.508	1.132	0.809	−0.952
C_2H_5OI	−1.751	−0.537	1.109	−2.115	−1.222	1.652
C_2H_3I	−1.133	1.843	−0.435	−1.499	1.142	0.115
SiC_3H_9I	4.345	4.352	−4.348	3.959	3.633	−3.776
OI_2	−29.279	−1.346	4.269	−28.801	−0.648	3.697
				B2PLYP-D3(BJ,abc)		
0	59.033	51.268	−55.016	4.455	3.216	−4.094
2	61.327	46.832	−53.617	5.962	0.190	−3.155
3	59.840	49.532	−54.486	4.985	2.032	−3.738
23	60.634	46.334	−53.023	5.506	−0.150	−2.756
24	60.856	46.800	−53.445	5.652	0.168	−3.040
25	60.843	46.398	−53.135	5.644	−0.106	−2.831
26	60.281	45.501	−52.228	5.275	−0.719	−2.222
34	57.013	51.639	−54.243	3.128	3.469	−3.575
35	60.668	47.815	−53.965	5.529	0.860	−3.388
234	60.300	46.254	−52.895	5.287	−0.205	−2.670
235	60.128	45.804	−52.479	5.174	−0.512	−2.391
236	59.677	45.130	−51.756	4.878	−0.972	−1.905
245	60.498	46.222	−52.948	5.418	−0.227	−2.705
246	59.778	45.528	−52.085	4.944	−0.701	−2.126
345	57.566	50.016	−53.659	3.492	2.362	−3.183
2356	59.012	44.455	−51.084	4.441	−1.433	−1.454
23456	58.760	44.061	−50.827	4.275	−1.702	−1.281
2345	59.893	45.489	−52.272	5.020	−0.727	−2.252
2346	59.310	44.971	−51.573	4.637	−1.080	−1.782
4	56.389	53.115	−54.708	2.719	4.477	−3.887
IF	37.326	37.326	−37.326	−9.802	−6.297	7.785
HI	52.819	52.819	−52.819	0.374	4.274	−2.619
CH_3I	41.707	41.708	−41.708	−6.925	−3.307	4.842
CNI	51.335	51.335	−51.335	−0.601	3.262	−1.623
C_2HI	58.526	58.526	−58.526	4.122	8.169	−6.451
CH_2I_2	45.597	42.765	−44.148	−4.370	−2.586	3.204
HOI	37.451	39.218	−38.345	−9.720	−5.006	7.100
C_3H_7I	47.950	44.207	−46.050	−2.824	−1.602	1.926
C_2H_5I	42.723	44.805	−43.770	−6.258	−1.193	3.457
CH_2ICl	43.904	42.348	−43.104	−5.482	−2.870	3.905
N_3I	39.477	42.853	−41.167	−8.389	−2.525	5.205

I_2	34.086	34.086	−34.086	−11.930	−8.508	9.960
C_2H_5OI	42.426	41.259	−41.809	−6.452	−3.614	4.774
C_2H_3I	55.442	48.364	−51.715	2.097	1.235	−1.878
SiC_3H_9I	49.471	49.478	−49.474	−1.825	1.995	−0.373
OI_2	90.199	−86.356	67.884	93.563	−27.158	12.735
B2PLYP-D3(BJ,abc)-DKH						
0	1.915	−0.150	−0.847	0.109	−0.858	0.347
2	2.342	−0.148	−1.017	0.528	−0.856	0.178
3	1.850	0.167	−0.976	0.044	−0.543	0.219
23	2.181	0.152	−1.101	0.369	−0.558	0.096
24	2.347	−0.093	−1.060	0.532	−0.801	0.136
25	2.253	0.168	−1.140	0.440	−0.542	0.057
26	2.605	−0.104	−1.129	0.787	−0.812	0.067
34	1.903	0.173	−1.011	0.096	−0.537	0.184
35	1.782	0.431	−1.077	−0.022	−0.281	0.119
234	2.205	0.244	−1.171	0.393	−0.466	0.026
235	2.075	0.417	−1.189	0.265	−0.295	0.008
236	2.428	0.246	−1.240	0.612	−0.464	−0.042
245	2.276	0.200	−1.178	0.463	−0.510	0.020
246	2.610	−0.039	−1.180	0.791	−0.748	0.017
345	1.812	0.414	−1.089	0.008	−0.298	0.108
2356	2.221	0.478	−1.272	0.409	−0.234	−0.073
23456	2.267	0.522	−1.325	0.454	−0.190	−0.126
2345	2.106	0.480	−1.246	0.296	−0.232	−0.048
2346	2.463	0.273	−1.281	0.647	−0.437	−0.083
4	1.933	−0.171	−0.852	0.126	−0.878	0.341
IF	3.399	3.399	−3.399	1.566	2.666	−2.175
HI	0.876	0.876	−0.876	−0.912	0.162	0.317
CH_3I	−0.928	−0.928	0.928	−2.684	−1.630	2.101
CNI	1.618	1.619	−1.619	−0.183	0.898	−0.416
C_2HI	0.976	0.976	−0.976	−0.814	0.260	0.219
CH_2I_2	0.126	0.471	−0.300	−1.648	−0.241	0.886
HOI	1.647	1.907	−1.779	−0.154	1.185	−0.574
C_3H_7I	−1.073	−1.913	1.499	−2.826	−2.608	2.665
C_2H_5I	−1.262	−0.960	1.111	−3.012	−1.662	2.281
CH_2ICl	0.402	0.205	−0.301	−1.377	−0.505	0.886
N_3I	2.855	2.907	−2.881	1.032	2.177	−1.664
I_2	2.356	2.356	−2.356	0.542	1.630	−1.145
C_2H_5OI	−1.034	−2.149	1.624	−2.788	−2.843	2.788
C_2H_3I	1.203	0.323	−0.740	−0.591	−0.388	0.452
SiC_3H_9I	1.601	1.607	−1.604	−0.200	0.887	−0.401
OI_2	69.142	−1.811	−5.613	69.689	−1.089	−6.730
B2PLYP-D3(BJ,abc)-X2C						
0	2.414	0.375	−1.359	0.126	−0.827	0.322
2	2.845	0.376	−1.532	0.547	−0.827	0.153
3	2.348	0.689	−1.486	0.061	−0.518	0.197
23	2.682	0.673	−1.613	0.388	−0.533	0.073
24	2.849	0.432	−1.575	0.551	−0.771	0.110
25	2.755	0.689	−1.653	0.459	−0.517	0.034
26	3.112	0.418	−1.644	0.808	−0.785	0.042
34	2.400	0.696	−1.522	0.112	−0.510	0.162
35	2.280	0.949	−1.586	−0.005	−0.261	0.099

234	2.705	0.767	−1.684	0.411	−0.440	0.003
235	2.575	0.935	−1.699	0.284	−0.274	−0.012
236	2.932	0.767	−1.753	0.632	−0.440	−0.065
245	2.777	0.723	−1.690	0.480	−0.484	−0.003
246	3.115	0.484	−1.695	0.811	−0.720	−0.008
345	2.309	0.932	−1.597	0.024	−0.277	0.089
2356	2.723	0.996	−1.783	0.428	−0.214	−0.094
23456	2.768	1.041	−1.836	0.472	−0.169	−0.147
2345	2.606	1.000	−1.756	0.313	−0.210	−0.068
2346	2.966	0.795	−1.795	0.665	−0.412	−0.106
4	2.431	0.356	−1.365	0.143	−0.847	0.316
IF	3.810	3.810	−3.810	1.491	2.566	−2.088
HI	1.431	1.431	−1.431	−0.836	0.216	0.252
CH_3I	−0.478	−0.478	0.478	−2.702	−1.670	2.129
CNI	2.133	2.133	−2.133	−0.149	0.910	−0.439
C_2HI	1.536	1.536	−1.536	−0.733	0.320	0.148
CH_2I_2	0.579	0.918	−0.750	−1.668	−0.291	0.921
HOI	2.069	2.339	−2.206	−0.211	1.113	−0.510
C_3H_7I	−0.588	−1.438	1.019	−2.809	−2.619	2.661
C_2H_5I	−0.802	−0.490	0.646	−3.019	−1.682	2.294
CH_2ICl	0.859	0.658	−0.756	−1.394	−0.548	0.916
N_3I	3.294	3.359	−3.327	0.986	2.121	−1.613
I_2	2.779	2.779	−2.779	0.482	1.547	−1.074
C_2H_5OI	−0.564	−1.693	1.161	−2.785	−2.871	2.800
C_2H_3I	1.699	0.837	−1.246	−0.573	−0.371	0.434
SiC_3H_9I	2.100	2.106	−2.103	−0.182	0.882	−0.409
OI_2	68.635	−2.481	−4.960	69.336	−1.253	−6.537
			B97-D3(BJ,abc)			
0	55.961	48.546	−52.125	5.590	2.701	−4.236
2	54.510	46.546	−50.274	4.607	1.319	−2.967
3	55.035	47.568	−51.156	4.962	2.026	−3.572
23	53.730	45.527	−49.364	4.079	0.614	−2.344
24	54.462	46.233	−50.123	4.575	1.102	−2.865
25	53.624	45.638	−49.362	4.007	0.691	−2.343
26	53.062	44.887	−48.608	3.627	0.172	−1.826
34	55.071	46.980	−50.900	4.987	1.619	−3.397
35	54.331	46.680	−50.341	4.486	1.412	−3.013
234	53.751	44.994	−49.134	4.093	0.246	−2.187
235	53.013	44.640	−48.542	3.594	0.001	−1.781
236	52.368	43.960	−47.790	3.157	−0.469	−1.266
245	53.667	45.148	−49.161	4.036	0.352	−2.205
246	52.962	44.618	−48.458	3.559	−0.014	−1.723
345	54.350	45.852	−49.952	4.499	0.839	−2.747
2356	51.813	42.896	−46.957	2.781	−1.204	−0.695
23456	51.873	42.162	−46.632	2.822	−1.712	−0.472
2345	53.102	43.886	−48.226	3.654	−0.521	−1.564
2346	52.357	43.448	−47.550	3.150	−0.823	−1.101
4	55.904	48.100	−51.896	5.551	2.393	−4.079
IF	32.978	32.978	−32.978	−9.971	−8.062	8.884
HI	53.384	53.384	−53.384	3.845	6.047	−5.099
CH_3I	43.402	43.402	−43.402	−2.913	−0.855	1.741
CNI	44.407	44.407	−44.407	−2.233	−0.160	1.052
C_2HI	54.001	54.001	−54.001	4.262	6.473	−5.521

CH_2I_2	41.246	42.898	−42.086	−4.373	−1.204	2.642
HOI	34.383	36.372	−35.389	−9.019	−5.715	7.231
C_3H_7I	49.422	45.633	−47.498	1.162	0.687	−1.066
C_2H_5I	43.897	46.555	−45.234	−2.578	1.325	0.486
CH_2ICl	39.988	42.068	−41.058	−5.225	−1.777	3.347
N_3I	37.655	38.731	−38.194	−6.804	−4.084	5.310
I_2	32.527	32.527	−32.527	−10.276	−8.374	9.193
C_2H_5OI	38.482	41.396	−40.022	−6.244	−2.242	4.057
C_2H_3I	47.988	49.660	−48.869	0.191	3.472	−2.005
SiC_3H_9I	52.095	52.101	−52.098	2.972	5.159	−4.217
OI_2	−87.927	−81.291	81.985	−27.232	−25.341	24.696
B97-D3(BJ,abc)-DKH						
0	−3.921	−1.013	2.417	−0.867	0.849	0.054
2	−4.033	−1.370	2.617	−0.983	0.486	0.258
3	−4.330	−1.101	2.653	−1.288	0.760	0.295
23	−4.277	−1.497	2.798	−1.234	0.356	0.444
24	−3.681	−1.542	2.553	−0.620	0.311	0.194
25	−4.464	−1.447	2.854	−1.427	0.407	0.501
26	−4.113	−1.580	2.733	−1.065	0.272	0.377
34	−4.010	−1.322	2.624	−0.958	0.534	0.266
35	−4.586	−1.153	2.796	−1.553	0.706	0.442
234	−3.967	−1.771	2.809	−0.914	0.077	0.456
235	−4.565	−1.525	2.941	−1.531	0.328	0.591
236	−4.379	−1.685	2.912	−1.339	0.165	0.561
245	−4.125	−1.670	2.827	−1.078	0.180	0.473
246	−3.784	−1.756	2.689	−0.726	0.092	0.333
345	−4.343	−1.463	2.852	−1.302	0.391	0.500
2356	−4.511	−1.777	3.022	−1.476	0.071	0.674
23456	−4.218	−2.013	3.028	−1.173	−0.170	0.680
2345	−4.275	−1.821	2.976	−1.232	0.026	0.627
2346	−4.062	−1.949	2.922	−1.012	−0.105	0.571
4	−3.576	−1.170	2.340	−0.511	0.689	−0.024
IF	−1.075	−1.075	1.075	2.070	0.787	−1.321
HI	0.487	0.487	−0.487	3.681	2.377	−2.920
CH_3I	−0.481	−0.480	0.481	2.683	1.392	−1.929
CNI	−4.957	−4.957	4.957	−1.936	−3.169	2.656
C_2HI	−3.520	−3.520	3.520	−0.453	−1.705	1.184
CH_2I_2	−4.809	−0.312	2.514	−1.783	1.564	0.154
HOI	−1.803	−1.356	1.576	1.319	0.500	−0.807
C_3H_7I	−0.835	−1.724	1.286	2.317	0.125	−1.104
C_2H_5I	−1.253	−0.492	0.871	1.885	1.380	−1.530
CH_2ICl	−3.795	−1.054	2.385	−0.737	0.808	0.021
N_3I	−1.263	0.126	0.568	1.875	2.010	−1.840
I_2	−0.045	−0.045	0.045	3.133	1.836	−2.376
C_2H_5OI	−5.230	−3.041	4.073	−2.218	−1.217	1.750
C_2H_3I	−5.610	0.390	2.449	−2.610	2.278	0.087
SiC_3H_9I	2.493	2.498	−2.496	5.751	4.427	−4.978
OI_2	−66.119	36.943	−26.160	−71.400	35.756	−24.372
B97-D3(BJ,abc)-X2C						
0	−3.456	−0.504	1.929	−0.849	0.880	0.029
2	−3.566	−0.863	2.128	−0.962	0.516	0.232
3	−3.866	−0.597	2.168	−1.270	0.786	0.272

23	−3.812	−0.995	2.313	−1.214	0.383	0.420
24	−3.214	−1.034	2.065	−0.600	0.343	0.167
25	−3.999	−0.944	2.369	−1.407	0.434	0.477
26	−3.643	−1.076	2.244	−1.041	0.301	0.350
34	−3.546	−0.818	2.140	−0.941	0.562	0.243
35	−4.124	−0.655	2.314	−1.535	0.728	0.421
234	−3.502	−1.268	2.324	−0.896	0.106	0.431
235	−4.101	−1.027	2.459	−1.511	0.350	0.569
236	−3.912	−1.183	2.426	−1.317	0.192	0.535
245	−3.660	−1.167	2.341	−1.058	0.209	0.449
246	−3.315	−1.251	2.201	−0.704	0.123	0.306
345	−3.881	−0.964	2.371	−1.285	0.414	0.480
2356	−4.047	−1.279	2.539	−1.455	0.095	0.651
23456	−3.754	−1.515	2.546	−1.154	−0.145	0.657
2345	−3.811	−1.323	2.495	−1.214	0.050	0.605
2346	−3.596	−1.448	2.437	−0.992	−0.076	0.546
4	−3.111	−0.660	1.852	−0.494	0.722	−0.050
IF	−0.691	−0.691	0.691	1.991	0.691	−1.234
HI	1.027	1.027	−1.027	3.756	2.433	−2.985
CH_3I	−0.041	−0.041	0.041	2.658	1.351	−1.896
CNI	−4.479	−4.479	4.479	−1.899	−3.149	2.628
C_2HI	−2.989	−2.989	2.989	−0.369	−1.639	1.109
CH_2I_2	−4.388	0.121	2.087	−1.806	1.514	0.190
HOI	−1.405	−0.948	1.174	1.258	0.431	−0.741
C_3H_7I	−0.362	−1.261	0.818	2.329	0.113	−1.104
C_2H_5I	−0.806	−0.033	0.417	1.873	1.359	−1.512
CH_2ICl	−3.366	−0.618	1.952	−0.756	0.765	0.052
N_3I	−0.838	0.543	0.147	1.839	1.942	−1.788
I_2	0.359	0.359	−0.359	3.069	1.756	−2.304
C_2H_5OI	−4.788	−2.600	3.632	−2.217	−1.244	1.764
C_2H_3I	−5.151	0.891	1.968	−2.589	2.295	0.068
SiC_3H_9I	2.983	2.989	−2.986	5.764	4.422	−4.982
OI_2	−67.276	36.396	−25.549	−71.794	35.510	−24.106
			B97M-D3(BJ,abc)			
0	54.140	44.213	−49.005	6.163	2.519	−4.503
2	52.741	41.801	−46.922	5.199	0.804	−3.041
3	53.243	43.344	−48.101	5.545	1.901	−3.869
23	51.904	40.908	−46.052	4.622	0.169	−2.431
24	52.621	41.548	−46.783	5.116	0.624	−2.944
25	51.888	41.009	−46.083	4.611	0.241	−2.453
26	51.310	39.776	−45.025	4.213	−0.636	−1.712
34	51.929	44.011	−47.847	4.640	2.375	−3.691
35	52.567	42.571	−47.354	5.079	1.351	−3.345
234	51.877	40.461	−45.858	4.604	−0.149	−2.296
235	51.208	40.139	−45.297	4.143	−0.377	−1.902
236	50.571	38.990	−44.265	3.704	−1.194	−1.178
245	51.874	40.563	−45.892	4.602	−0.076	−2.319
246	51.163	39.571	−44.905	4.112	−0.781	−1.627
345	52.077	42.235	−46.984	4.742	1.113	−3.085
2356	49.952	38.057	−43.474	3.278	−1.857	−0.623
23456	50.002	37.354	−43.176	3.313	−2.357	−0.415
2345	51.265	39.451	−45.014	4.182	−0.866	−1.704
2346	50.528	38.536	−44.058	3.675	−1.517	−1.033

4	51.860	45.824	−48.760	4.592	3.664	−4.331
IF	29.278	29.278	−29.278	−10.961	−8.099	9.333
HI	49.436	49.436	−49.436	2.922	6.231	−4.805
CH_3I	40.148	40.148	−40.148	−3.475	−0.371	1.709
CNI	41.860	41.860	−41.860	−2.295	0.846	0.509
C_2HI	51.729	51.729	−51.729	4.502	7.862	−6.413
CH_2I_2	40.383	39.421	−39.889	−3.313	−0.888	1.891
HOI	30.769	32.397	−31.593	−9.934	−5.881	7.709
C_3H_7I	46.334	42.071	−44.170	0.786	0.996	−1.112
C_2H_5I	40.478	43.481	−41.989	−3.247	1.999	0.418
CH_2ICl	38.723	39.226	−38.982	−4.456	−1.027	2.527
N_3I	33.437	35.582	−34.511	−8.096	−3.617	5.663
I_2	26.806	26.806	−26.806	−12.664	−9.856	11.067
C_2H_5OI	37.952	39.190	−38.606	−4.987	−1.052	2.791
C_2H_3I	46.931	45.393	−46.122	1.197	3.358	−2.480
SiC_3H_9I	47.493	47.497	−47.495	1.585	4.853	−3.444
OI_2	−6.883	−79.041	71.492	26.385	−27.278	20.273
			B97M-D3(BJ,abc)-DKH			
0	−3.771	−2.888	3.314	−0.100	0.439	−0.172
2	−3.929	−3.657	3.784	−0.264	−0.356	0.315
3	−4.189	−2.904	3.521	−0.534	0.423	0.043
23	−4.242	−3.696	3.951	−0.589	−0.396	0.488
24	−3.648	−3.799	3.727	0.028	−0.503	0.256
25	−4.362	−3.651	3.983	−0.713	−0.350	0.520
26	−4.077	−4.230	4.160	−0.417	−0.949	0.704
34	−3.932	−3.109	3.508	−0.267	0.211	0.028
35	−4.455	−2.881	3.634	−0.810	0.446	0.159
234	−3.976	−3.918	3.946	−0.312	−0.627	0.482
235	−4.543	−3.643	4.062	−0.901	−0.342	0.603
236	−4.401	−4.237	4.312	−0.754	−0.956	0.861
245	−4.075	−3.856	3.959	−0.416	−0.562	0.496
246	−3.792	−4.370	4.104	−0.121	−1.094	0.646
345	−4.249	−3.165	3.688	−0.596	0.152	0.215
2356	−4.602	−4.232	4.400	−0.963	−0.951	0.953
23456	−4.316	−4.456	4.392	−0.665	−1.183	0.944
2345	−4.280	−3.900	4.079	−0.628	−0.608	0.620
2346	−4.109	−4.466	4.301	−0.450	−1.193	0.851
4	−3.523	−3.033	3.271	0.158	0.289	−0.217
IF	−3.090	−3.090	3.090	0.607	0.230	−0.404
HI	−1.223	−1.223	1.223	2.546	2.161	−2.339
CH_3I	−1.487	−1.486	1.486	2.272	1.889	−2.066
CNI	−5.811	−5.811	5.811	−2.218	−2.584	2.415
C_2HI	−4.120	−4.120	4.120	−0.462	−0.835	0.663
CH_2I_2	−3.752	−1.686	2.699	−0.079	1.682	−0.810
HOI	−3.571	−3.405	3.487	0.108	−0.096	0.007
C_3H_7I	−1.495	−2.819	2.167	2.263	0.510	−1.360
C_2H_5I	−2.324	−1.226	1.772	1.402	2.158	−1.770
CH_2ICl	−3.177	−1.634	2.383	0.517	1.736	−1.137
N_3I	−2.487	−1.915	2.201	1.233	1.445	−1.326
I_2	−3.616	−3.616	3.616	0.061	−0.314	0.141
C_2H_5OI	−3.816	−2.874	3.318	−0.147	0.454	−0.168
C_2H_3I	−4.971	−1.438	3.109	−1.346	1.939	−0.384
SiC_3H_9I	0.939	0.943	−0.941	4.790	4.401	−4.581

OI_2	−9.553	3.270	−1.929	−13.732	−0.044	1.608
			B97M-D3(BJ,abc)-X2C			
0	−3.292	−2.372	2.816	−0.082	0.469	−0.197
2	−3.448	−3.145	3.287	−0.243	−0.326	0.288
3	−3.711	−2.393	3.026	−0.515	0.448	0.020
23	−3.763	−3.188	3.457	−0.569	−0.370	0.463
24	−3.166	−3.286	3.229	0.048	−0.472	0.229
25	−3.883	−3.143	3.488	−0.693	−0.324	0.496
26	−3.594	−3.722	3.664	−0.394	−0.920	0.677
34	−3.455	−2.597	3.013	−0.250	0.238	0.005
35	−3.979	−2.375	3.142	−0.792	0.466	0.139
234	−3.497	−3.410	3.451	−0.294	−0.599	0.458
235	−4.066	−3.139	3.571	−0.881	−0.320	0.581
236	−3.922	−3.731	3.818	−0.732	−0.930	0.836
245	−3.597	−3.347	3.465	−0.397	−0.534	0.471
246	−3.309	−3.862	3.608	−0.100	−1.064	0.619
345	−3.773	−2.659	3.197	−0.578	0.174	0.195
2356	−4.125	−3.730	3.910	−0.943	−0.928	0.930
23456	−3.839	−3.955	3.901	−0.647	−1.159	0.922
2345	−3.803	−3.396	3.588	−0.610	−0.585	0.599
2346	−3.629	−3.961	3.808	−0.430	−1.166	0.826
4	−3.043	−2.516	2.772	0.176	0.321	−0.242
IF	−2.704	−2.704	2.704	0.525	0.128	−0.313
HI	−0.674	−0.674	0.674	2.623	2.217	−2.406
CH_3I	−1.037	−1.037	1.037	2.248	1.843	−2.031
CNI	−5.323	−5.323	5.323	−2.181	−2.568	2.388
C_2HI	−3.578	−3.578	3.578	−0.377	−0.771	0.588
CH_2I_2	−3.312	−1.246	2.259	−0.103	1.628	−0.772
HOI	−3.169	−2.994	3.080	0.045	−0.171	0.075
C_3H_7I	−1.010	−2.347	1.688	2.276	0.495	−1.360
C_2H_5I	−1.867	−0.756	1.308	1.390	2.133	−1.752
CH_2ICl	−2.732	−1.187	1.937	0.497	1.689	−1.104
N_3I	−2.055	−1.494	1.774	1.196	1.373	−1.271
I_2	−3.216	−3.216	3.216	−0.003	−0.399	0.215
C_2H_5OI	−3.355	−2.418	2.860	−0.147	0.422	−0.152
C_2H_3I	−4.496	−0.929	2.616	−1.326	1.955	−0.403
SiC_3H_9I	1.438	1.443	−1.441	4.806	4.395	−4.586
OI_2	−10.298	2.611	−1.260	−13.960	−0.223	1.801
			BP86-D3(BJ,abc)			
0	55.123	47.314	−51.083	5.739	2.846	−4.391
2	53.693	45.072	−49.107	4.764	1.280	−3.025
3	54.155	46.301	−50.076	5.079	2.139	−3.695
23	52.920	43.994	−48.170	4.237	0.528	−2.378
24	53.723	44.693	−48.962	4.784	1.016	−2.925
25	52.767	44.124	−48.155	4.133	0.618	−2.367
26	52.322	43.177	−47.339	3.829	−0.042	−1.804
34	54.255	45.638	−49.813	5.147	1.675	−3.513
35	53.427	45.377	−49.228	4.582	1.493	−3.109
234	53.011	43.359	−47.923	4.299	0.084	−2.207
235	52.178	43.068	−47.313	3.731	−0.119	−1.786
236	51.638	42.177	−46.486	3.363	−0.741	−1.215
245	52.887	43.555	−47.951	4.214	0.221	−2.227

246	52.299	42.846	−47.196	3.814	−0.274	−1.705
345	53.506	44.460	−48.825	4.636	0.853	−2.830
2356	51.105	41.053	−45.631	3.000	−1.525	−0.623
23456	51.237	40.247	−45.305	3.089	−2.088	−0.399
2345	52.340	42.215	−46.983	3.842	−0.714	−1.558
2346	51.697	41.588	−46.243	3.403	−1.152	−1.046
4	55.036	46.911	−50.863	5.679	2.564	−4.239
IF	31.401	31.401	−31.401	−10.432	−8.264	9.209
HI	51.196	51.196	−51.196	3.062	5.556	−4.469
CH_3I	42.872	42.872	−42.872	−2.612	−0.256	1.283
CNI	43.237	43.237	−43.237	−2.363	−0.001	1.031
C_2HI	52.832	52.832	−52.832	4.177	6.698	−5.599
CH_2I_2	40.318	42.278	−41.316	−4.353	−0.670	2.358
HOI	32.888	35.064	−33.989	−9.418	−5.707	7.420
C_3H_7I	48.715	44.773	−46.714	1.370	1.072	−1.372
C_2H_5I	43.104	46.028	−44.575	−2.454	1.948	0.106
CH_2ICl	38.721	41.363	−40.080	−5.442	−1.309	3.212
N_3I	36.363	37.784	−37.074	−7.049	−3.808	5.289
I_2	31.411	31.411	−31.411	−10.424	−8.257	9.202
C_2H_5OI	36.468	40.898	−38.809	−6.977	−1.633	4.090
C_2H_3I	46.566	48.593	−47.635	−0.094	3.739	−2.008
SiC_3H_9I	51.713	51.719	−51.716	3.414	5.921	−4.828
OI_2	−75.040	−78.731	78.344	−19.315	−24.779	23.227
			BP86-D3(BJ,abc)-DKH			
0	−4.433	−1.844	3.094	−0.697	0.574	0.070
2	−4.543	−2.404	3.405	−0.812	0.001	0.391
3	−4.882	−1.965	3.367	−1.164	0.451	0.351
23	−4.786	−2.581	3.613	−1.064	−0.181	0.605
24	−4.130	−2.629	3.339	−0.382	−0.230	0.322
25	−5.012	−2.517	3.681	−1.299	−0.115	0.675
26	−4.575	−2.812	3.614	−0.845	−0.418	0.607
34	−4.513	−2.250	3.346	−0.780	0.158	0.330
35	−5.167	−2.053	3.543	−1.460	0.360	0.533
234	−4.422	−2.940	3.640	−0.686	−0.549	0.633
235	−5.102	−2.646	3.791	−1.393	−0.248	0.789
236	−4.841	−2.986	3.831	−1.122	−0.596	0.830
245	−4.614	−2.806	3.658	−0.886	−0.412	0.652
246	−4.185	−3.039	3.566	−0.440	−0.650	0.557
345	−4.876	−2.437	3.614	−1.158	−0.033	0.606
2356	−4.959	−3.121	3.958	−1.244	−0.734	0.961
23456	−4.610	−3.418	3.967	−0.881	−1.039	0.970
2345	−4.756	−3.022	3.839	−1.033	−0.633	0.838
2346	−4.467	−3.307	3.841	−0.733	−0.925	0.841
4	−4.035	−2.043	3.012	−0.284	0.370	−0.015
IF	−2.293	−2.293	2.293	1.526	0.114	−0.756
HI	−1.166	−1.166	1.166	2.697	1.269	−1.918
CH_3I	−0.732	−0.731	0.731	3.149	1.714	−2.366
CNI	−5.834	−5.834	5.834	−2.153	−3.514	2.896
C_2HI	−4.375	−4.375	4.375	−0.637	−2.019	1.391
CH_2I_2	−5.439	−0.660	3.000	−1.743	1.788	−0.026
HOI	−2.919	−2.314	2.613	0.876	0.092	−0.426
C_3H_7I	−1.172	−2.200	1.694	2.691	0.210	−1.374
C_2H_5I	−1.690	−0.714	1.199	2.153	1.732	−1.884

CH_2ICl	−4.661	−1.456	3.012	−0.934	0.971	−0.014
N_3I	−1.907	−0.786	1.346	1.927	1.658	−1.732
I_2	−0.821	−0.821	0.821	3.056	1.622	−2.274
C_2H_5OI	−6.587	−3.233	4.815	−2.935	−0.849	1.844
C_2H_3I	−6.614	−0.315	3.296	−2.964	2.141	0.278
SiC_3H_9I	2.558	2.564	−2.561	6.567	5.091	−5.761
OI_2	−65.831	4.630	2.742	−72.313	2.281	5.948
BP86-D3(BJ,abc)-X2C						
0	−3.970	−1.338	2.608	−0.679	0.604	0.045
2	−4.078	−1.901	2.920	−0.791	0.030	0.365
3	−4.421	−1.463	2.885	−1.146	0.475	0.329
23	−4.323	−2.082	3.130	−1.045	−0.156	0.581
24	−3.664	−2.126	2.853	−0.363	−0.200	0.296
25	−4.550	−2.019	3.199	−1.279	−0.091	0.652
26	−4.108	−2.312	3.129	−0.822	−0.390	0.580
34	−4.051	−1.749	2.864	−0.763	0.184	0.308
35	−4.707	−1.557	3.064	−1.442	0.380	0.513
234	−3.958	−2.441	3.158	−0.667	−0.521	0.610
235	−4.641	−2.152	3.312	−1.373	−0.227	0.767
236	−4.377	−2.488	3.349	−1.100	−0.570	0.805
245	−4.151	−2.307	3.176	−0.867	−0.385	0.628
246	−3.718	−2.539	3.081	−0.419	−0.621	0.531
345	−4.416	−1.941	3.136	−1.141	−0.012	0.586
2356	−4.496	−2.628	3.479	−1.224	−0.712	0.938
23456	−4.148	−2.925	3.488	−0.863	−1.015	0.948
2345	−4.294	−2.528	3.360	−1.015	−0.611	0.816
2346	−4.003	−2.811	3.360	−0.713	−0.898	0.816
4	−3.571	−1.536	2.526	−0.267	0.401	−0.040
IF	−1.914	−1.914	1.914	1.447	0.016	−0.668
HI	−0.632	−0.632	0.632	2.773	1.324	−1.984
CH_3I	−0.293	−0.292	0.293	3.124	1.670	−2.332
CNI	−5.359	−5.359	5.359	−2.116	−3.496	2.868
C_2HI	−3.847	−3.847	3.847	−0.552	−1.955	1.316
CH_2I_2	−5.020	−0.228	2.575	−1.766	1.735	0.011
HOI	−2.524	−1.910	2.214	0.816	0.020	−0.360
C_3H_7I	−0.700	−1.738	1.227	2.703	0.195	−1.373
C_2H_5I	−1.244	−0.255	0.747	2.140	1.707	−1.865
CH_2ICl	−4.235	−1.022	2.582	−0.953	0.926	0.018
N_3I	−1.485	−0.373	0.928	1.891	1.587	−1.679
I_2	−0.420	−0.420	0.420	2.992	1.539	−2.201
C_2H_5OI	−6.149	−2.792	4.375	−2.933	−0.879	1.859
C_2H_3I	−6.159	0.184	2.817	−2.943	2.155	0.259
SiC_3H_9I	3.049	3.055	−3.052	6.580	5.083	−5.764
OI_2	−66.786	3.991	3.414	−72.501	2.102	6.136

Tab. S21: Parametrised nuclear quadrupole moments Q_{eff} in the inertial ($Q_{\text{eff,in}}$) and in the nuclear principal axis system ($Q_{\text{eff,nuc}}$), obtained from a linear regression of the experimental diagonal nuclear quadrupole coupling tensor components against theory. Details of this approach, along with information on the different levels of theory functionals used for calculating the field gradients, are given in Sec. 2.3 of the main text. Functionals are combined with the x2c-TZVPPall basis set, unless otherwise stated. In some cases, the basis set was decontracted. This is indicated by "d.". The level of theory proposed by Bailey is abbreviated as "Bailey". The uncertainties of the slopes obtained from the regressions were used in order to calculate the uncertainties of Q_{eff}. Experimental uncertainties have been neglected. Additionally, the ratios Q/Q_{eff} have been calculated, along with their errors, using a Gaussian error propagation. Here, Q is the nuclear quadrupole moment of the isolated iodine atom, taken from Ref. [9].

Method	$Q_{\text{eff,in}}$	$Q/Q_{\text{eff,in}}$	$Q_{\text{eff,nuc}}$	$Q/Q_{\text{eff,nuc}}$
PBE/def2-SVP	−38.81(57)	0.017 73(26)	−38.90(59)	0.017 69(27)
Bailey	−0.751(10)	0.917(12)	−0.762(11)	0.903(13)
B3LYP-D3(BJ,abc)/d.	−0.7713(90)	0.892(10)	−0.7769(73)	0.8858(83)
B3LYP-D3(BJ,abc)-DKH2/d.	−0.6859(63)	1.0035(93)	−0.6889(45)	0.9990(65)
B3LYP-D3(BJ,abc)-X2C/d.	−0.6826(62)	1.0083(92)	−0.6857(44)	1.0037(65)
B3LYP-D3(BJ,abc)	−0.461(19)	1.491(60)	−0.456(20)	1.509(66)
B3LYP-D3(BJ,abc)-DKH2	−0.6859(63)	1.0035(93)	−0.6889(45)	0.9990(65)
B3LYP-D3(BJ,abc)-X2C	−0.6826(62)	1.0083(92)	−0.6857(44)	1.0037(65)
B2PLYP-D3(BJ,abc)	−0.459(18)	1.500(58)	−0.452(22)	1.522(74)
B2PLYP-D3(BJ,abc)-DKH2	−0.6773(65)	1.0162(97)	−0.6760(75)	1.018(11)
B2PLYP-D3(BJ,abc)-X2C	−0.6740(63)	1.0211(96)	−0.6728(74)	1.023(11)
B97-D3(BJ,abc)	−0.469(19)	1.467(58)	−0.466(18)	1.477(58)
B97-D3(BJ,abc)-DKH2	−0.703(16)	0.979(22)	−0.7101(96)	0.969(13)
B97-D3(BJ,abc)-X2C	−0.700(16)	0.984(22)	−0.7068(95)	0.974(13)
B97M-D3(BJ,abc)	−0.480(21)	1.434(62)	−0.474(22)	1.452(66)
B97M-D3(BJ,abc)-DKH2	−0.7113(88)	0.968(12)	−0.7145(50)	0.9633(68)
B97M-D3(BJ,abc)-X2C	−0.7078(87)	0.972(12)	−0.7111(49)	0.9679(67)
BP86-D3(BJ,abc)	−0.473(19)	1.455(58)	−0.469(19)	1.467(60)
BP86-D3(BJ,abc)-DKH2	−0.7081(90)	0.972(12)	−0.7151(96)	0.962(13)
BP86-D3(BJ,abc)-X2C	−0.7048(89)	0.977(12)	−0.7118(95)	0.967(13)

Tab. S22: The experimental nuclear quadrupole constants χ_{xx}, χ_{yy} and χ_{zz} in the nuclear principal axis system. The nomenclature of the fluoroiodobenzenes is described in Fig. 1 of the main text.

Molecule	χ_{xx} / MHz	χ_{yy} / MHz	χ_{zz} / MHz
0	913.219(12)	978.821(12)	−1892.0398(46)
2	943.2217(75)	1071.9225(79)	−2015.1442(59)
3	927.0716(34)	1002.0007(42)	−1929.0724(40)
4	935.25(11)	987.60(11)	−1922.85(11)
23	956.7357(39)	1088.5210(46)	−2045.2566(46)
24	965.3478(51)	1076.5305(51)	−2041.8783(53)
25	955.148(20)	1093.016(19)	−2048.164(11)
26	971.6561(47)	1163.1885(47)	−2134.8446(54)
34	947.396(29)	1007.949(29)	−1955.345(57)
35	941.153(11)	1025.969(11)	−1967.122(11)
234	977.9736(47)	1090.5685(52)	−2068.5421(49)
235	969.596(16)	1111.227(16)	−2080.822(27)
236	984.342(65)	1176.774(65)	−2161.116(84)
245	976.367(14)	1096.230(14)	−2072.597(16)
246	993.982(14)	1165.962(14)	−2159.943(16)
345	960.90(11)	1030.56(11)	−1991.46(17)
2345	990.5555(32)	1112.9205(33)	−2103.4759(31)
2346	1006.1144(30)	1179.0703(30)	−2185.1846(40)
2356	998.328(32)	1194.012(32)	−2192.339(38)
23456	1020.278(13)	1196.244(13)	−2216.522(10)

4.2 Figures

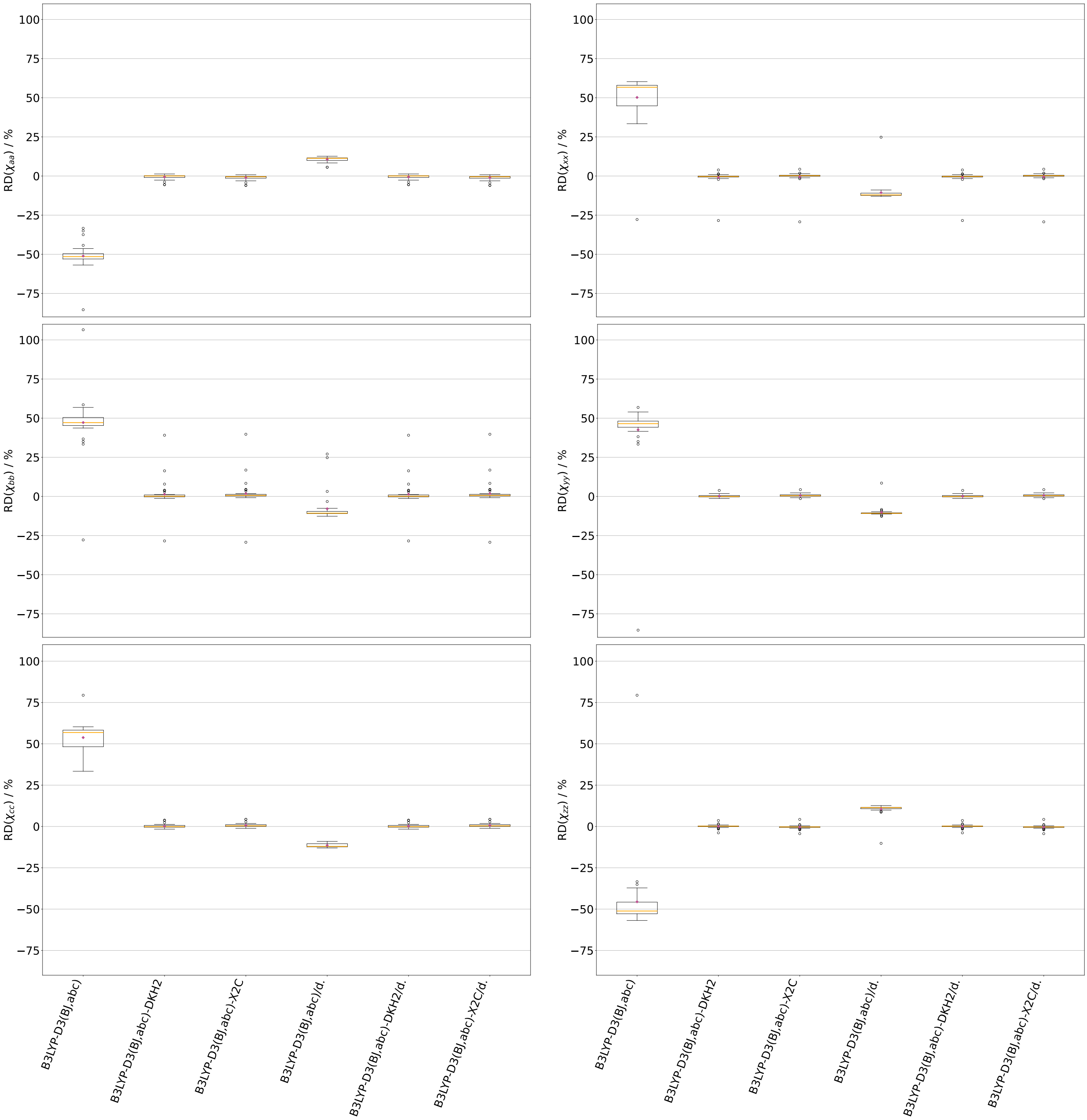

Fig. S5: Boxplots of the relative deviations RD, defined according to Eq. 6 of the main text, of the three diagonal components of the nuclear quadrupole coupling tensor in the nuclear principal axis system, χ_{xx}, χ_{yy} and χ_{zz}, in the right column and of the three diagonal components of the nuclear quadrupole coupling tensor in the inertial principal axis system, χ_{aa}, χ_{bb} and χ_{cc}, in the left column. B3LYP with and without relativistic corrections, DKH2 and X2C, was paired with the x2c-TZVPPall basis set. In some cases, the basis set was decontracted, indicated by “d.”.

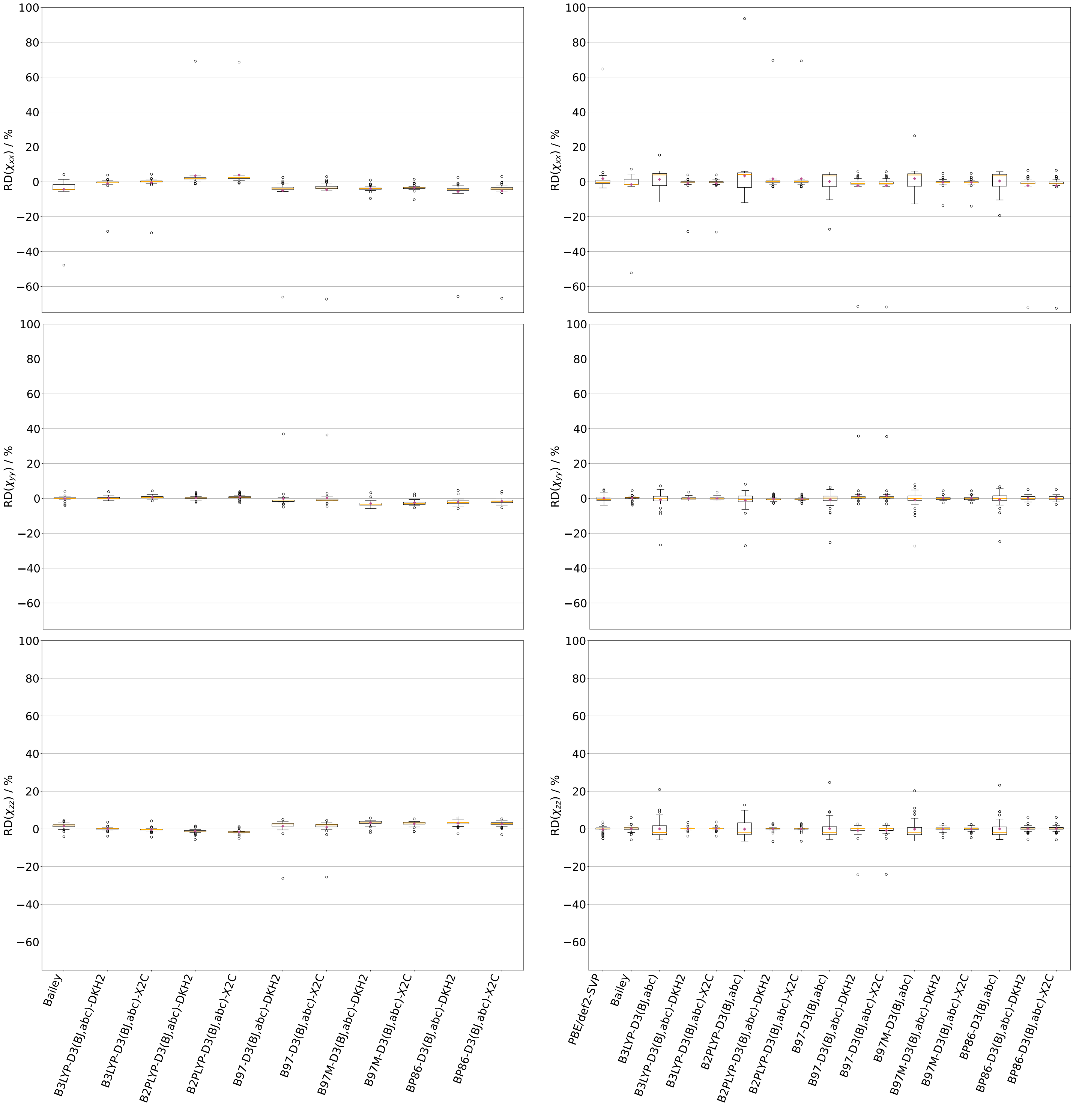

Fig. S6: Boxplots of the relative deviations RD, defined according to Eq. 6, of the three diagonal components of the nuclear quadrupole coupling tensor in the nuclear principal axis system, χ_{xx}, χ_{yy} and χ_{zz}. The plots in the right-handed column use parametrised results, obtained from linear regressions using all three diagonal components of all molecules. Numerous different functionals have been employed for the theoretical calculations of the electric field gradients, paired with the x2c-TZVPPall basis set, unless otherwise stated. "Bailey" denotes a special level of theory, explained in Sec. 2.3 of the main text.

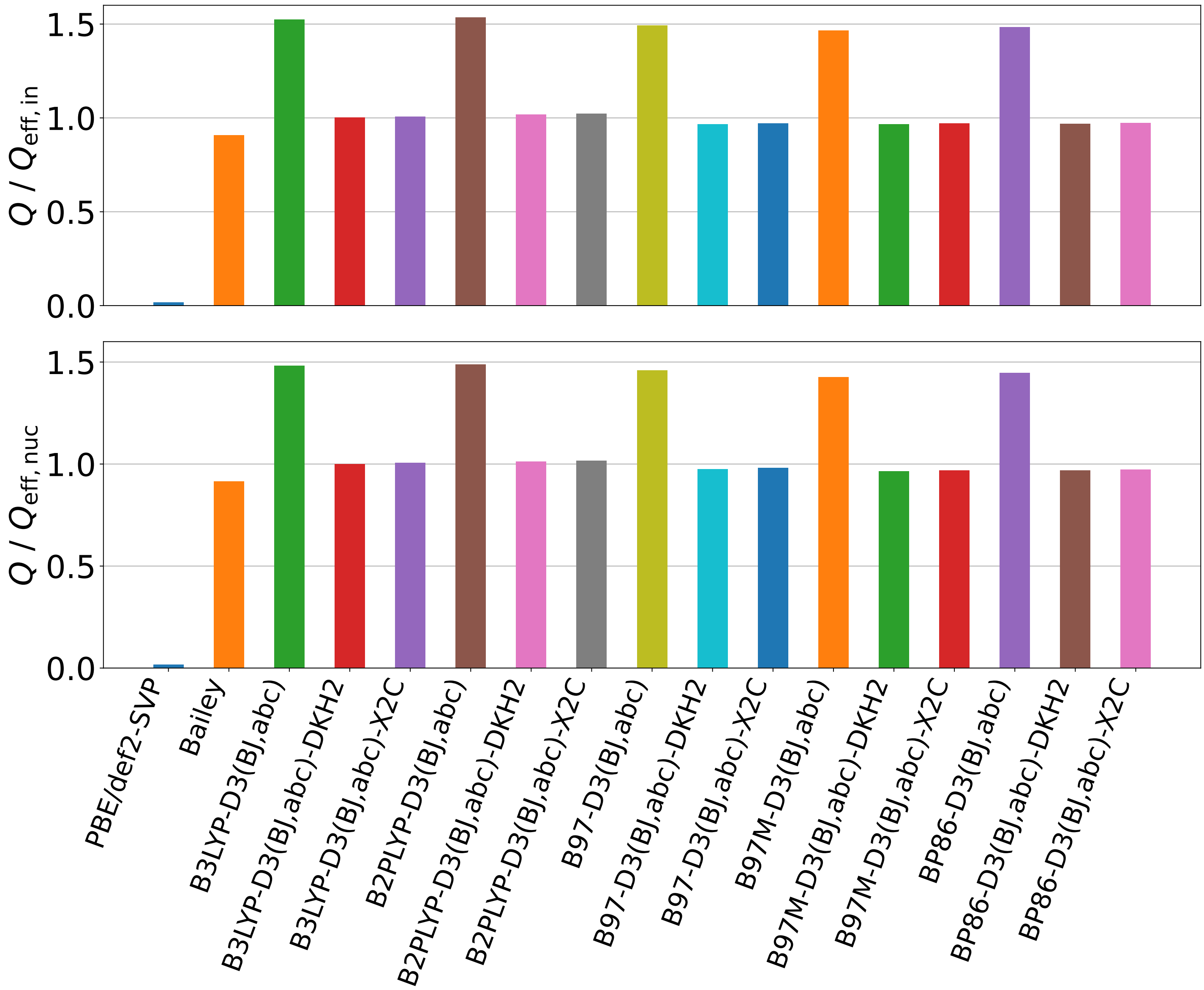

Fig. S7: Ratios Q/Q_{eff} of the nuclear quadrupole moment Q of the isolated iodine atom, and the parametrised nuclear quadrupole moments Q_{eff}, obtained from a linear regression of the experimental diagonal nuclear quadrupole coupling tensor components, for different levels of theory. Both, the results in the inertial principle axis system $Q/Q_{\text{eff,in}}$ (top) and in the nuclear principal axis system $Q/Q_{\text{eff,nuc}}$ (bottom) are shown. Details of this approach along with information on the different levels of theory functionals used for calculating the field gradients, are given in Sec. 2.3 of the main text. Unless otherwise stated, functionals are combined with the x2c-TZVPPall basis set. The level of theory proposed by Bailey is abbreviated as "Bailey". Exact values are given in Tab. S21.

5 Computational Details and Exemplary Input Files

Tab. S23: Overview of the different computational methods used for geometry optimisations and frequency calculations in this work. Information on the program used, the method employed, the basis set, any necessary/possible dispersion corrections, the functional class for density functionals and the type of frequency calculation is provided. SCS refers to spin component scaling, rs to range-separated and VPT2 to vibrational perturbation theory of second order. ORCA 6.0.1 is abbreviated as ORCA, and Gaussian 16 (Rev. C.01) refers to G16. TZ refers to the def2-TZVP basis set and maTZ to the ma-def2-TZVP basis set.

Program	Method	Basis set	Dispersion	Functional class	Frequency
G16	B3LYP	TZ	D3(BJ)	hybrid	VPT2
G16	PBE0	TZ	D3(BJ)	hybrid	VPT2
G16	CAM-B3LYP	TZ	D3(BJ)	rs hybrid	VPT2
G16	LC-ωPBE	TZ	D3(BJ)	rs hybrid	VPT2
G16	M06-2X	TZ	—	meta hybrid	VPT2
G16	B2PLYP	TZ	D3(BJ)	double hybrid	VPT2
G16	DSD-PBEP86	TZ	D3(BJ)	SCS double hybrid	VPT2
G16	MP2	TZ	—	—	VPT2
ORCA	B3LYP	maTZ	D3(BJ,abc)	hybrid	harmonic

Tab. S24: Overview of the different computational methods employed for point calculations of the electric field gradients in this work. The underlying geometries were optimised at the B3LYP-D3(BJ,abc)/ma-def2-TZVP level of theory. ORCA 6.0.1 was used throughout. Information is provided on the method employed, the basis set, any necessary/possible dispersion corrections, the functional class for density functionals, and the type of relativistic correction. SCS refers to spin component scaling and rs to range-separated. Regarding the relativistic corrections, DKH2 refers to the second order Douglas-Kroll-Hess transformation, while X2C refers to the exact two-component theory. All calculations were also performed without relativistic corrections. A f-polarization function with a coefficient of 0.4 was added to the 6-311G(d,p) basis set, resulting in 6-311G(df,p).

Method	Basis set	Dispersion	Functional class	Relativistic correction
PBE	def2-SVP	—	GGA	—
BP86	x2c-TZVPPall	D3(BJ,abc)	GGA	DKH2/X2C
B97-M	x2c-TZVPPall	D3(BJ,abc)	meta-GGA	DKH2/X2C
B1LYP	6-311G(df,p)	—	hybrid	—
B3LYP	x2c-TZVPPall	D3(BJ,abc)	hybrid	DKH2/X2C
CAM-B3LYP	x2c-TZVPPall	D3(BJ,abc)	rs hybrid	DKH2/X2C
B2PLYP	x2c-TZVPPall	D3(BJ,abc)	double hybrid	DKH2/X2C

5.1 ORCA

Tab. S25: Exemplary input files for the ORCA 6.0.1 For different functional/basis set combinations, the respective keywords in the first line were exchanged. The specific type of calculation is given in the left column and the corresponding input on the right side.

Type of calculation	Input

geometry optimisation and analytical frequency calculation	`!B3LYP D3BJ ABC ma-def2-TZVP SCFConv10`
	`VeryTightOpt NORI NOCOSX Freq DefGrid3 Mass2016`
	`%geom`
	` MaxIter 500`
	` ENFORCESTRICTCONVERGENCE true`
	` TolE 1e-8`
	` TolRMSG 2e-6`
	` TolMaxG 4e-6`
	` TolRMSD 4e-5`
	` TolMaxD 6e-5`
	`end`
	`%scf`
	` MaxIter 1500`
	`end`

EFG calculation with X2C, picture change effects and finite nucleus model	`!B3LYP D3BJ ABC x2c-TZVPPall VeryTightSCF`
	`NORI NOCOSX Freq DefGrid3 Mass2016`
	`%rel`
	` method X2C`
	` PictureChange 2`
	` FiniteNuc true`
	`end`
	`%eprnmr`
	` nuclei = all I fgrad`
	`end`

5.2 MOLPRO

Tab. S26: Exemplary input files for the MOLPRO 2024.1 For different functional/basis set combinations, the respective keywords were exchanged. The specific type of calculation is given in the left column and the corresponding input on the right side.

Type of calculation	Input

IBBA analysis with DKH2 and finite nucleus model	`basis=cc-pVTZ-DK`
	`set,DKHO=2,fnuc=1`
	`gthresh,OPTSTEP=6.d-5,OPTGRAD=1.d-6,ENERGY=1.d-12,`
	`ZERO=1.d-16,twoint=1.d-14`
	`orient,NOORIENT`
	`symmetry,nosym`
	`MASS,ISO`
	`geomtyp=xyz`
	`angstrom`
	`geometry=Test_start.xyz`
	`{hf;accu,16}`

```
{rks,B3LYP,disp=[d3,BJ,ABC]}
{IBBA, bonds=1}
{POP}
```

5.3 Gaussian

Tab. S27: Exemplary input files for the Gaussian 16 (Rev. C.01) calculations. For different functional/basis set combinations, the respective keywords were exchanged. The specific type of calculation is given in the left column and the corresponding input on the right side. The geometry optimisation and VPT2 calculations were carried out separately from each other.

Type of calculation	Input
geometry optimisation	`# B3LYP def2tzvp Int=SuperFine empiricaldispersion=gd3bj output=pickett` `# Opt=VeryTight`

VPT2 calculation	`# B3LYP def2tzvp Int=SuperFine empiricaldispersion=gd3bj output=pickett`
	`# Geom=Checkpoint`
	`# Freq=(Anharmonic,ReadAnharm)`
	`Print=(NMOrder=AscNoIrrep,ITop=Ir)`
	`Resonances=No11Res`

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