Supplementary Material

Benchmarking quantum chemical methods for accurate gas-phase structure predictions of carbonyl compounds: The case of ethyl butyrate

Lilian W. Sutikdja[a], Ha Vinh Lam Nguyen†[b,c], Dragan Jelisavac[a],

Wolfgang Stahl[a]†† and Halima Mouhib†[d]

[a.] *Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, D-52074 Aachen, Germany.*

[b.] *Univ Paris Est Creteil and Université Paris Cité, CNRS, LISA, F-94010 Créteil, France.*

[c.] *Institut Universitaire de France (IUF), F-75231 Paris cedex 05, France*

[d.] *Department of Computer Science, VU Bioinformatics, Vrije Universiteit Amsterdam, De Boelelaan 1111, 1081 HV Amsterdam, The Netherlands*

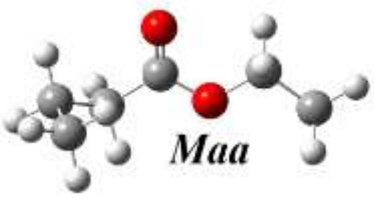
† Corresponding authors. Emails: lam.nguyen@lisa.ipsl.fr and h.mouhib@vu.nl.

†† Deceased.

Table S-1. The rotational constants *A*, *B*, *C* (in **G**Hz), the dipole moment components μ_a, μ_b, μ_c (in Debye), and energies $E_{rel.}$ (in kJ·mol^{-1}) relative to E = –385.3378749 Hartree of the 14 conformers of ethyl butyrate predicted at the MP2/6-311++G(d,p) level level of theory.

Conf.	**Notation**	***A***	***B***	***C***	$\lvert\mu_a\rvert$	$\lvert\mu_b\rvert$	$\lvert\mu_c\rvert$	$E_{rel.}$
I	Maa	4.572	0.941	0.916	–0.63	–1.66	0.61	0
II	MaP	3.722	1.130	1.047	–0.25	–0.21	–1.67	0.62
III	PPa	3.082	1.200	1.035	0.20	–2.08	–0.98	0.73
IV	MPa	3.085	1.199	1.035	–0.20	–2.08	–0.98	0.73
V	MaM	5.033	0.980	0.971	0.37	–0.05	–1.66	0.74
VI	PPP	2.999	1.335	1.185	0.32	1.17	–1.75	0.89
VII	MPM	2.999	1.335	1.184	–0.32	1.17	–1.75	0.89
VIII	PPM	4.012	1.114	1.057	0.25	–1.80	1.06	1.52
IX	MPP	4.011	1.114	1.057	–0.25	–1.80	1.06	1.53
X	aaa	6.333	0.806	0.731	–0.47	0.00	0.00	2.29
XI	aPa	3.949	0.945	0.816	0.06	–2.19	0.36	2.67
XII	aPP	3.920	1.004	0.931	0.42	–1.73	1.07	2.89
XIII	aaP	6.068	0.851	0.811	–0.46	–1.83	–0.02	2.90
XIV	aPM	5.302	0.908	0.847	0.41	–1.96	0.37	3.54
Expt. C_1		**5.238**	**0.904**	**0.869**				
Expt. C_s		**6.328**	**0.807**	**0.732**				

Conformer I:

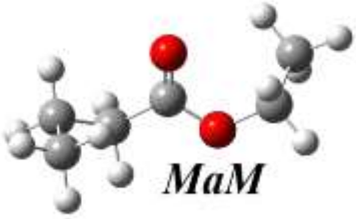


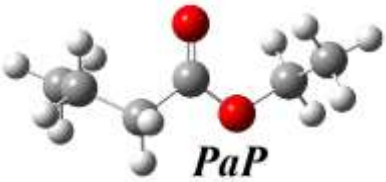
Conformer II:

Conformer III:

Conformer IV:

Conformer V:





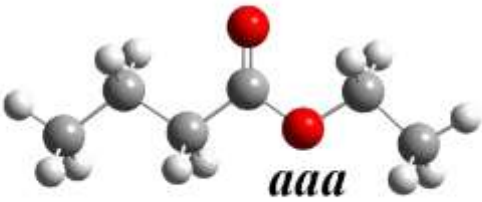
Conformer VI:

Conformer VII:

Conformer VIII:

Conformer IX:

Conformer X:



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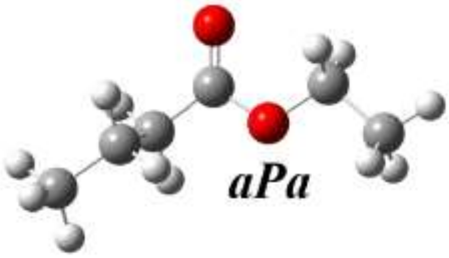

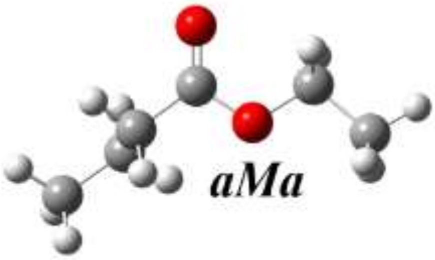

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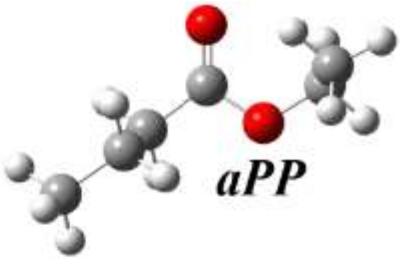

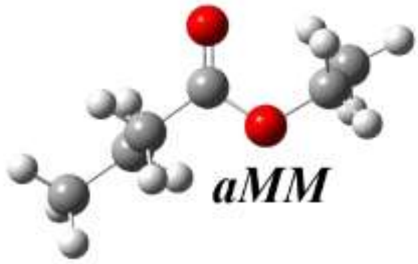

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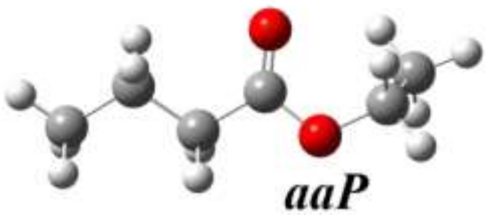

Conformer XIV:

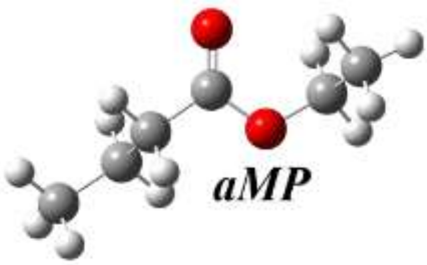

Table S-2a. Geometry parameters in the principal axes of inertia of the two observed conformers Maa and aaa of ethyl butyrate calculated at the MP2/6-311++G(d,p) level of theory. The atoms are numbered according to Figure 1.

	Conformer Maa			Conformer aaa		
	a **/Å**	***b*** **/Å**	***c*** **/Å**	***a*** **/Å**	***b*** **/Å**	***c*** **/Å**
C1	0.100084	0.355162	0.287577	–0.051775	0.312215	0.000079
O2	0.187770	1.463707	–0.198127	–0.074327	1.524901	0.000037
O3	–1.043569	–0.366838	0.298279	–1.166471	–0.456142	0.000069
C4	1.225530	–0.383047	0.977053	1.190868	–0.548272	0.000194
H5	1.216747	–0.054910	2.024099	1.142067	–1.205586	0.876760
H6	1.007515	–1.455051	0.970595	1.141857	–1.206180	–0.875910
C7	2.579968	–0.083778	0.333446	2.479906	0.266829	–0.000217
H8	3.366529	–0.530951	0.951147	2.488264	0.922749	–0.876447
H9	2.739669	0.998739	0.332315	2.488435	0.923358	0.875553
C10	2.671068	–0.624841	–1.093831	3.716713	–0.631476	–0.000031
H11	1.917414	–0.158963	–1.735809	4.635240	–0.037814	–0.000336
H12	3.653041	–0.420432	–1.530155	3.732117	–1.275683	0.885291
H13	2.513078	–1.708591	–1.108786	3.731933	–1.276308	–0.884902
C14	–2.182266	0.294512	–0.294067	–2.409042	0.278007	0.000015
H15	–2.370371	1.225900	0.247111	–2.440553	0.919667	0.884836
H16	–1.943346	0.547767	–1.330468	–2.440407	0.919788	–0.884720
C17	–3.350907	–0.662906	–0.199544	–3.528132	–0.741349	–0.000145
H18	–3.564403	–0.909620	0.843045	–3.472814	–1.375199	0.887880
H19	–4.240466	–0.199762	–0.636360	–4.493226	–0.226294	–0.000169
H20	–3.137768	–1.586387	–0.742829	–3.472691	–1.375054	–0.888267

Table S-2b. Geometry parameters in the principal axes of inertia of the two observed conformers Maa and aaa of ethyl butyrate calculated at the MP2/cc-pVDZ level of theory. The atoms are numbered according to Figure 1.

	Conformer Maa			**Conformer aaa**		
	***a* /Å**	***b* /Å**	***c* /Å**	***a* /Å**	***b* /Å**	***c* /Å**
C1	–0.079734	0.097693	–0.295994	–0.053269	0.307366	–0.000330
O2	–0.226350	1.295108	–0.456839	–0.071694	1.523666	0.000116
O3	1.113547	–0.482216	–0.011948	–1.170542	–0.464045	–0.000198
C4	–1.170106	–0.949745	–0.410335	1.190734	–0.556577	–0.000095
H5	–0.997956	–1.481618	–1.364150	1.138841	–1.222285	0.880658
H6	–1.020982	–1.696734	0.388433	1.139002	–1.222518	–0.880675
C7	–2.573346	–0.343242	–0.364507	2.477934	0.264554	–0.000059
H8	–3.305400	–1.122848	–0.639176	2.479703	0.929294	–0.881024
H9	–2.640001	0.450675	–1.127771	2.479491	0.929548	0.880713
C10	–2.919914	0.232623	1.010641	3.724928	–0.620877	0.000214
H11	–2.225351	1.044702	1.278915	4.645632	–0.015080	0.000228
H12	–3.942563	0.644341	1.023233	3.748957	–1.271954	0.891122
H13	–2.860856	–0.547650	1.789753	3.749159	–1.272221	–0.890492
C14	2.219638	0.443438	0.067643	–2.407011	0.281999	0.000091
H15	2.315100	0.978140	–0.892333	–2.437467	0.933952	0.889209
H16	2.006793	1.195866	0.845383	–2.437759	0.934145	–0.888875
C17	3.455368	–0.373628	0.389392	–3.533318	–0.732710	0.000168
H18	3.641605	–1.120710	–0.397988	–3.476596	–1.374041	0.893628
H19	4.334776	0.286581	0.462192	–4.506417	–0.215423	0.000389
H20	3.332005	–0.900784	1.348390	–3.476896	–1.373841	–0.893454

Table S-3. The rotational constants *A*, *B*, *C* (in MHz) of conformer Maa of ethyl butyrate calculated at different levels of theory and their deviations to the experimental values (calc.–exp.) Δ*A*, Δ*B*, and Δ*C*, respectively (in MHz). The Θ angle (in degree) is also given.

Level of theory	***A***	**Δ*A***	***B***	**Δ*B***	***C***	**Δ*C***	***Θ***
B3LYP/6-31G(d,p)	5291.8	53.7	891.1	–12.7	853.2	–16.1	16.0
B3LYP/6-31+G(d,p)	4992.8	–245.3	893.3	–10.5	863.8	–5.5	23.5
B3LYP/6-31++G(d,p)	5012.6	–225.5	892.4	–11.4	862.5	–6.8	23.0
B3LYP/6-311G(d,p)	5373.7	135.6	888.0	–15.8	848.4	–20.9	14.1
B3LYP/6-311+G(d,p)	5071.4	–166.7	892.9	–10.9	862.2	–7.1	22.0
B3LYP/6-311++G(d,p)	5079.9	–158.2	892.7	–11.1	861.7	–7.6	21.8
B3LYP/6-311G(2d,2p)	5427.3	189.2	889.2	–14.6	849.3	–20.0	13.5
B3LYP/6-311+G(2d,2p)	5160.0	–78.1	892.9	–10.9	860.8	–8.5	20.4
B3LYP/6-311++G(2d,2p)	5159.9	–78.2	892.9	–10.9	860.8	–8.5	20.4
B3LYP/6-311G(df,pd)	5378.3	140.2	890.6	–13.2	851.2	–18.1	14.3
B3LYP/6-311+G(df,pd)	5077.4	–160.7	895.5	–8.3	864.9	–4.4	22.3
B3LYP/6-311++G(df,pd)	5077.5	–160.6	895.6	–8.2	864.9	–4.4	22.2
B3LYP/6-311G(2df,2pd)	5449.8	211.7	889.5	–14.3	848.7	–20.6	12.9
B3LYP/6-311+G(2df,2pd)	5179.6	–58.5	893.2	–10.6	860.3	–9.0	20.0
B3LYP/6-311++G(2df,2pd)	5178.8	–59.3	893.2	–10.6	860.4	–8.9	20.0
B3LYP/6-311G(3df,3pd)	5410.6	172.5	890.3	–13.5	850.6	–18.7	14.0
B3LYP/6-311+G(3df,3pd)	5147.3	–90.8	894.8	–9.0	863.0	–6.3	20.9
B3LYP/6-311++G(3df,3pd)	5145.6	–92.5	894.9	–8.9	863.1	–6.2	21.0
B3LYP/cc-pVDZ	5404.6	166.5	886.9	–16.9	845.4	–23.9	12.6
B3LYP/aug-cc-pVDZ	5127.7	–110.4	889.8	–14.0	857.3	–12.0	20.5
B3LYP/cc-pVTZ	5270.1	32.0	891.3	–12.5	855.8	–13.5	17.5
B3LYP/aug-cc-pVTZ	5155.6	–82.5	893.3	–10.5	861.0	–8.3	20.5
B3LYP-D3/6-31G(d,p)	5352.3	114.2	896.7	–7.1	855.5	–13.8	14.0
B3LYP-D3/6-31+G(d,p)	5095.6	–142.5	897.5	–6.3	865.1	–4.2	20.7
B3LYP-D3/6-31++G(d,p)	5114.8	–123.3	896.8	–7.0	863.8	–5.5	20.2
B3LYP-D3/6-311G(d,p)	5439.0	200.9	893.8	–10.0	850.7	–18.6	12.1
B3LYP-D3/6-311+G(d,p)	5165.3	–72.8	897.7	–6.1	864.0	–5.3	19.3
B3LYP-D3/6-311++G(d,p)	5166.1	–72.0	897.7	–6.1	863.9	–5.4	19.3
B3LYP-D3/6-311G(2d,2p)	5466.9	228.8	895.4	–8.4	852.8	–16.5	12.1
B3LYP-D3/6-311+G(2d,2p)	5231.8	–6.3	898.3	–5.5	863.4	–5.9	18.3
B3LYP-D3/6-311++G(2d,2p)	5230.7	–7.4	898.3	–5.5	863.5	–5.8	18.3
B3LYP-D3/6-311G(df,pd)	5444.1	206.0	896.3	–7.5	853.4	–15.9	12.3
B3LYP-D3/6-311+G(df,pd)	5170.5	–67.6	900.2	–3.6	866.7	–2.6	19.7
B3LYP-D3/6-311++G(df,pd)	5166.7	–71.4	900.4	–3.4	866.9	–2.4	19.7
B3LYP-D3/6-311G(2df,2pd)	5485.4	247.3	895.8	–8.0	852.5	–16.8	11.6
B3LYP-D3/6-311+G(2df,2pd)	5251.1	13.0	898.7	–5.1	863.0	–6.3	17.9
B3LYP-D3/6-311++G(2df,2pd)	5249.4	11.3	898.7	–5.1	863.1	–6.2	17.9
B3LYP-D3/6-311G(3df,3pd)	5456.0	217.9	896.5	–7.3	854.0	–15.3	12.5
B3LYP-D3/6-311+G(3df,3pd)	5226.2	–11.9	900.1	–3.7	865.4	–3.9	18.6
B3LYP-D3/6-311++G(3df,3pd)	5224.3	–13.8	900.2	–3.6	865.5	–3.8	18.6
B3LYP-D3/cc-pVDZ	5456.4	218.3	892.7	–11.1	848.1	–21.2	10.8
B3LYP-D3/aug-cc-pVDZ	5194.2	–43.9	895.5	–8.3	860.4	–8.9	18.5
B3LYP-D3/cc-pVTZ	5339.8	101.7	897.0	–6.8	858.3	–11.0	15.5
B3LYP-D3/aug-cc-pVTZ	5236.7	–1.4	898.6	–5.2	863.3	–6.0	18.2

B3LYP-D3BJ/6-31G(d,p)	5236.6	–1.5	900.4	–3.4	863.7	–5.6	17.3
B3LYP-D3BJ/6-31+G(d,p)	4916.1	–322.0	904.9	1.1	877.5	8.2	25.4
B3LYP-D3BJ/6-31++G(d,p)	4930.8	–307.3	904.1	0.3	876.4	7.1	25.0
B3LYP-D3BJ/6-311G(d,p)	5337.1	99.0	896.7	–7.1	857.6	–11.7	15.1
B3LYP-D3BJ/6-311+G(d,p)	4999.4	–238.7	904.0	0.2	875.2	5.9	23.8
B3LYP-D3BJ/6-311++G(d,p)	5010.8	–227.3	903.6	–0.2	874.5	5.2	23.5
B3LYP-D3BJ/6-311G(2d,2p)	5380.0	141.9	898.1	–5.7	859.0	–10.3	14.7
B3LYP-D3BJ/6-311+G(2d,2p)	5092.8	–145.3	903.5	–0.3	873.1	3.8	22.1
B3LYP-D3BJ/6-311++G(2d,2p)	5093.5	–144.6	903.4	–0.4	873.1	3.8	22.1
B3LYP-D3BJ/6-311G(df,pd)	5336.5	98.4	899.4	–4.4	860.7	–8.6	15.5
B3LYP-D3BJ/6-311+G(df,pd)	5001.5	–236.6	906.8	3.0	878.2	8.9	24.1
B3LYP-D3BJ/6-311++G(df,pd)	5001.3	–236.8	906.9	3.1	878.3	9.0	24.1
B3LYP-D3BJ/6-311G(2df,2pd)	5406.4	168.3	898.2	–5.6	858.1	–11.2	14.0
B3LYP-D3BJ/6-311+G(2df,2pd)	5114.4	–123.7	903.6	–0.2	872.5	3.2	21.6
B3LYP-D3BJ/6-311++G(2df,2pd)	5113.3	–124.8	903.7	–0.1	872.5	3.2	21.6
B3LYP-D3BJ/6-311G(3df,3pd)	5368.9	130.8	899.1	–4.7	860.1	–9.2	15.2
B3LYP-D3BJ/6-311+G(3df,3pd)	5073.1	–165.0	905.8	2.0	875.9	6.6	22.7
B3LYP-D3BJ/6-311++G(3df,3pd)	5071.6	–166.5	905.8	2.0	876.0	6.7	22.7
B3LYP-D3BJ/cc-pVDZ	5366.4	128.3	895.2	–8.6	854.4	–14.9	13.6
B3LYP-D3BJ/aug-cc-pVDZ	5054.5	–183.6	900.7	–3.1	870.2	0.9	22.4
B3LYP-D3BJ/cc-pVTZ	5219.1	–19.0	901.0	–2.8	866.6	–2.7	18.8
B3LYP-D3BJ/aug-cc-pVTZ	5087.4	–150.7	904.0	0.2	873.5	4.2	22.2
CAM-B3LYP-D3BJ/6-311G(d,p)	5475.1	237.0	902.5	–1.3	860.2	–9.1	12.5
CAM-B3LYP-D3BJ/6-311+G(d,p)	5208.2	–29.9	906.2	2.4	872.8	3.5	19.6
CAM-B3LYP-D3BJ/6-311++G(d,p)	5210.5	–27.6	906.1	2.3	872.6	3.3	19.5
CAM-B3LYP-D3BJ/aug-cc-pVDZ	5233.2	–4.9	903.8	0.0	869.4	0.1	18.9
CAM-B3LYP-D3BJ/aug-cc-pVTZ	5265.4	27.3	907.4	3.6	873.1	3.8	18.8
CAM-B3LYP-D3BJ/cc-pVDZ	5500.8	262.7	901.3	–2.5	857.3	–12.0	11.2
CAM-B3LYP-D3BJ/cc-pVTZ	5375.1	137.0	905.7	1.9	867.8	–1.5	16.0
CCSD/cc-pVDZ	5397.0	158.9	894.4	–9.4	852.0	–17.3	12.6
M06-2X/6-31G(d,p)	5476.6	238.5	907.5	3.7	864.0	–5.3	12.1
M06-2X/6-31+G(d,p)	5343.3	105.2	906.4	2.6	867.6	–1.7	15.7
M06-2X/6-31++G(d,p)	5356.8	118.7	905.9	2.1	866.7	–2.6	15.3
M06-2X/6-311G(d,p)	5523.8	285.7	905.6	1.8	861.4	–7.9	11.2
M06-2X/6-311+G(d,p)	5361.9	123.8	907.5	3.7	869.0	–0.3	15.6
M06-2X/6-311++G(d,p)	5359.5	121.4	907.6	3.8	869.1	–0.2	15.6
M06-2X/6-311G(2d,2p)	5570.8	332.7	906.6	2.8	862.2	–7.1	10.7
M06-2X/6-311+G(2d,2p)	5422.0	183.9	908.1	4.3	868.7	–0.6	14.7
M06-2X/6-311++G(2d,2p)	5418.6	180.5	908.1	4.3	868.8	–0.5	14.8
M06-2X/6-311G(df,pd)	5525.6	287.5	907.5	3.7	863.6	–5.7	11.4
M06-2X/6-311+G(df,pd)	5368.7	130.6	909.3	5.5	870.9	1.6	15.7
M06-2X/6-311++G(df,pd)	5361.9	123.8	909.6	5.8	871.4	2.1	15.9
M06-2X/6-311G(2df,2pd)	5579.6	341.5	906.6	2.8	861.8	–7.5	10.4
M06-2X/6-311+G(2df,2pd)	5436.2	198.1	907.9	4.1	867.9	–1.4	14.3
M06-2X/6-311++G(2df,2pd)	5433.4	195.3	907.9	4.1	868.1	–1.2	14.4
M06-2X/6-311G(3df,3pd)	5552.1	314.0	907.3	3.5	863.4	–5.9	11.3
M06-2X/6-311+G(3df,3pd)	5427.4	189.3	908.8	5.0	869.3	0.0	14.6
M06-2X/6-311++G(3df,3pd)	5426.7	188.6	908.8	5.0	869.3	0.0	14.6

M06-2X/cc-pVDZ	5550.5	312.4	904.9	1.1	859.4	–9.9	10.1
M06-2X/aug-cc-pVDZ	5379.1	141.0	906.1	2.3	866.9	–2.4	15.2
M06-2X/cc-pVTZ	5476.5	238.4	907.3	3.5	865.9	–3.4	13.2
M06-2X/aug-cc-pVTZ	5413.0	174.9	908.0	4.2	868.9	–0.4	14.9
MN15/6-31G(d,p)	5424.1	186.0	907.3	3.5	865.8	–3.5	13.4
MN15/6-31+G(d,p)	5294.1	56.0	905.0	1.2	868.0	–1.3	16.8
MN15/6-31++G(d,p)	5307.6	69.5	904.5	0.7	867.1	–2.2	16.4
MN15/6-311G(d,p)	5504.1	266.0	906.7	2.9	863.6	–5.7	11.7
MN15/6-311+G(d,p)	5342.9	104.8	908.5	4.7	871.0	1.7	16.0
MN15/6-311++G(d,p)	5348.4	110.3	908.4	4.6	870.7	1.4	15.9
MN15/6-311G(2d,2p)	5562.1	324.0	908.8	5.0	865.2	–4.1	10.9
MN15/6-311+G(2d,2p)	5418.2	180.1	910.0	6.2	871.2	1.9	14.8
MN15/6-311++G(2d,2p)	5418.1	180.0	910.0	6.2	871.1	1.8	14.8
MN15/6-311G(df,pd)	5509.0	270.9	909.6	5.8	866.6	–2.7	11.9
MN15/6-311+G(df,pd)	5349.3	111.2	911.3	7.5	874.0	4.7	16.3
MN15/6-311++G(df,pd)	5348.5	110.4	911.4	7.6	874.2	4.9	16.3
MN15/6-311G(2df,2pd)	5580.2	342.1	909.1	5.3	864.8	–4.5	10.5
MN15/6-311+G(2df,2pd)	5436.4	198.3	910.3	6.5	870.9	1.6	14.4
MN15/6-311++G(2df,2pd)	5436.7	198.6	910.3	6.5	870.8	1.5	14.4
MN15/6-311G(3df,3pd)	5535.6	297.5	909.8	6.0	866.9	–2.4	11.7
MN15/6-311+G(3df,3pd)	5430.6	192.5	910.5	6.7	871.4	2.1	14.5
MN15/6-311++G(3df,3pd)	5433.1	195.0	910.5	6.7	871.2	1.9	14.5
MN15/cc-pVDZ	5521.3	283.2	904.2	0.4	860.2	–9.1	10.8
MN15/aug-cc-pVDZ	5370.1	132.0	906.2	2.4	867.6	–1.7	15.4
MN15/cc-pVTZ	5467.9	229.8	910.0	6.2	869.2	–0.1	13.4
MN15/aug-cc-pVTZ	5421.6	183.5	911.1	7.3	872.1	2.8	14.7
PBE0/6-31G(d,p)	5166.2	–71.9	891.7	–12.1	856.0	–13.3	17.9
PBE0/6-31+G(d,p)	4840.1	–398.0	895.9	–7.9	868.3	–1.0	26.3
PBE0/6-31++G(d,p)	4857.1	–381.0	895.1	–8.7	867.2	–2.1	25.9
PBE0/6-311G(d,p)	5254.7	16.6	888.7	–15.1	851.0	–18.3	16.0
PBE0/6-311+G(d,p)	4906.4	–331.7	896.1	–7.7	867.9	–1.4	25.1
PBE0/6-311++G(d,p)	4918.4	–319.7	895.7	–8.1	867.2	–2.1	24.8
PBE0/6-311G(2d,2p)	5325.3	87.2	888.9	–14.9	850.3	–19.0	14.8
PBE0/6-311+G(2d,2p)	5013.6	–224.5	894.4	–9.4	864.7	–4.6	23.0
PBE0/6-311++G(2d,2p)	5016.4	–221.7	894.3	–9.5	864.5	–4.8	22.9
PBE0/6-311G(df,pd)	5263.1	25.0	891.3	–12.5	853.7	–15.6	16.2
PBE0/6-311+G(df,pd)	4912.0	–326.1	898.7	–5.1	870.6	1.3	25.4
PBE0/6-311++G(df,pd)	4923.5	–314.6	898.5	–5.3	870.2	0.9	25.1
PBE0/6-311G(2df,2pd)	5350.7	112.6	889.4	–14.4	849.8	–19.5	14.1
PBE0/6-311+G(2df,2pd)	5039.8	–198.3	894.6	–9.2	864.1	–5.2	22.5
PBE0/6-311++G(2df,2pd)	5040.4	–197.7	894.6	–9.2	864.0	–5.3	22.4
PBE0/6-311G(3df,3pd)	5318.0	79.9	890.2	–13.6	851.5	–17.8	15.2
PBE0/6-311+G(3df,3pd)	4995.1	–243.0	897.0	–6.8	867.7	–1.6	23.6
PBE0/6-311++G(3df,3pd)	4992.9	–245.2	897.1	–6.7	867.8	–1.5	23.6
PBE0/cc-pVDZ	5278.3	40.2	887.3	–16.5	848.0	–21.3	14.7
PBE0/aug-cc-pVDZ	4971.3	–266.8	891.9	–11.9	862.1	–7.2	23.4
PBE0/cc-pVTZ	5149.3	–88.8	891.7	–12.1	858.1	–11.2	19.4
PBE0/aug-cc-pVTZ	5001.3	–236.8	895.1	–8.7	865.3	–4.0	23.3
PBE0-D3/6-31G(d,p)	5134.8	–103.3	896.0	–7.8	860.7	–8.6	18.5

PBE0-D3/6-31+G(d,p)	4767.4	–470.7	903.0	–0.8	876.7	7.4	27.9
PBE0-D3/6-31++G(d,p)	4785.9	–452.2	901.8	–2.0	875.3	6.0	27.4
PBE0-D3/6-311G(d,p)	5233.5	–4.6	892.7	–11.1	855.0	–14.3	16.3
PBE0-D3/6-311+G(d,p)	4846.9	–391.2	902.3	–1.5	875.3	6.0	26.3
PBE0-D3/6-311++G(d,p)	4862.7	–375.4	901.7	–2.1	874.4	5.1	25.9
PBE0-D3/6-311G(2d,2p)	5298.4	60.3	892.9	–10.9	854.4	–14.9	15.2
PBE0-D3/6-311+G(2d,2p)	4957.0	–281.1	900.1	–3.7	871.6	2.3	24.2
PBE0-D3/6-311++G(2d,2p)	4960.3	–277.8	900.0	–3.8	871.4	2.1	24.0
PBE0-D3/6-311G(df,pd)	5239.2	1.1	895.3	–8.5	857.8	–11.5	16.5
PBE0-D3/6-311+G(df,pd)	4857.9	–380.2	904.8	1.0	877.8	8.5	26.5
PBE0-D3/6-311++G(df,pd)	4862.4	–375.7	904.7	0.9	877.7	8.4	26.4
PBE0-D3/6-311G(2df,2pd)	5321.4	83.3	893.4	–10.4	854.0	–15.3	14.6
PBE0-D3/6-311+G(2df,2pd)	4983.2	–254.9	900.3	–3.5	871.0	1.7	23.5
PBE0-D3/6-311++G(2df,2pd)	4983.7	–254.4	900.2	–3.6	870.9	1.6	23.5
PBE0-D3/6-311G(3df,3pd)	5293.2	55.1	894.2	–9.6	855.5	–13.8	15.6
PBE0-D3/6-311+G(3df,3pd)	4936.8	–301.3	902.9	–0.9	874.9	5.6	24.8
PBE0-D3/6-311++G(3df,3pd)	4935.6	–302.5	903.0	–0.8	874.9	5.6	24.8
PBE0-D3/cc-pVDZ	5259.9	21.8	891.0	–12.8	851.6	–17.7	14.8
PBE0-D3/aug-cc-pVDZ	4912.0	–326.1	897.9	–5.9	869.4	0.1	24.6
PBE0-D3/cc-pVTZ	5115.6	–122.5	896.3	–7.5	863.2	–6.1	20.1
PBE0-D3/aug-cc-pVTZ	4943.1	–295.0	901.0	–2.8	872.5	3.2	24.5
ωB97X-D/6-31G(d,p)	5307.3	69.2	903.6	–0.2	865.5	–3.8	16.3
ωB97X-D/6-31+G(d,p)	5074.7	–163.4	905.8	2.0	874.9	5.6	22.2
ωB97X-D/6-31++G(d,p)	5085.2	–152.9	905.3	1.5	874.1	4.8	22.0
ωB97X-D/6-311G(d,p)	5128.0	–110.1	906.4	2.6	874.7	5.4	21.3
ωB97X-D/6-311+G(d,p)	5133.3	–104.8	906.2	2.4	874.4	5.1	21.2
ωB97X-D/6-311++G(d,p)	5367.6	129.5	902.0	–1.8	862.8	–6.5	15.2
ωB97X-D/6-311G(2d,2p)	5429.9	191.8	902.6	–1.2	862.7	–6.6	14.1
ωB97X-D/6-311+G(2d,2p)	5208.1	–30.0	905.9	2.1	872.9	3.6	20.0
ωB97X-D/6-311++G(2d,2p)	5206.5	–31.6	905.9	2.1	873.0	3.7	20.0
ωB97X-D/6-311G(df,pd)	5363.2	125.1	904.6	0.8	865.9	–3.4	15.6
ωB97X-D/6-311+G(df,pd)	5128.6	–109.5	908.9	5.1	877.4	8.1	21.7
ωB97X-D/6-311++G(df,pd)	5124.1	–114.0	909.1	5.3	877.8	8.5	21.8
ωB97X-D/6-311G(2df,2pd)	5579.6	341.5	906.6	2.8	861.8	–7.5	10.4
ωB97X-D/6-311+G(2df,2pd)	5436.2	198.1	907.9	4.1	867.9	–1.4	14.3
ωB97X-D/6-311++G(2df,2pd)	5433.4	195.3	907.9	4.1	868.1	–1.2	14.4
ωB97X-D/6-311G(3df,3pd)	5397.3	159.2	904.2	0.4	864.9	–4.4	15.1
ωB97X-D/6-311+G(3df,3pd)	5201.7	–36.4	907.5	3.7	874.5	5.2	20.2
ωB97X-D/6-311++G(3df,3pd)	5199.8	–38.3	907.5	3.7	874.6	5.3	20.2
ωB97X-D/aug-cc-pVDZ	5150.7	–87.4	903.3	–0.5	870.7	1.4	20.6
ωB97X-D/aug-cc-pVTZ	5200.0	–38.1	906.4	2.6	873.3	4.0	20.1
ωB97X-D/cc-pVDZ	5400.9	162.8	899.5	–4.3	858.6	–10.7	13.6
ωB97X-D/cc-pVTZ	5281.6	43.5	904.6	0.8	869.1	–0.2	18.0
MP2/6-31G(d,p)	5179.1	–59.0	912.1	8.3	876.2	6.9	19.4
MP2/6-31+G(d,p)	4655.1	–583.0	931.6	27.8	907.2	37.9	32.5
MP2/6-31++G(d,p)	4561.3	–676.8	938.4	34.6	912.6	43.3	34.8
MP2/6-311G(d,p)	5002.1	–236.0	919.0	15.2	890.1	20.8	24.3

MP2/6-311+G(d,p)	4550.3	–687.8	943.2	39.4	917.9	48.6	35.2
MP2/6-311++G(d,p)	4571.6	–666.5	941.4	37.6	916.5	47.2	34.7
MP2/6-311G(2d,2p)	5336.1	98.0	911.4	7.6	872.5	3.2	15.9
MP2/6-311+G(2d,2p)	5011.1	–227.0	919.1	15.3	890.6	21.3	24.4
MP2/6-311++G(2d,2p)	5002.8	–235.3	919.3	15.5	891.0	21.7	24.6
MP2/6-311G(df,pd)	5037.7	–200.4	925.9	22.1	897.3	28.0	24.4
MP2/6-311+G(df,pd)	4539.2	–698.9	954.4	50.6	928.0	58.7	36.6
MP2/6-311++G(df,pd)	4539.8	–698.3	954.3	50.5	927.9	58.6	36.5
MP2/6-311G(2df,2pd)	5377.1	139.0	915.9	12.1	875.8	6.5	15.2
MP2/6-311+G(2df,2pd)	5041.1	–197.0	923.5	19.7	894.5	25.2	24.0
MP2/6-311++G(2df,2pd)	5029.3	–208.8	923.9	20.1	895.2	25.9	24.4
MP2/6-311G(3df,3pd)	5305.6	67.5	916.9	13.1	878.9	9.6	17.0
MP2/6-311+G(3df,3pd)	4978.4	–259.7	926.3	22.5	899.0	29.7	25.4
MP2/6-311++G(3df,3pd)	4978.8	–259.3	926.3	22.5	898.9	29.6	25.4
MP2/cc-pVDZ	5259.6	21.5	904.4	0.6	865.6	–3.7	16.2
MP2/aug-cc-pVDZ	4695.1	–543.0	924.4	20.6	901.4	32.1	30.9
MP2/cc-pVTZ	5132.5	–105.6	919.1	15.3	886.9	17.6	21.4
MP2/aug-cc-pVTZ	4978.8	–259.3	924.2	20.4	896.5	27.2	25.1
Expt.	**5238.1**		**903.8**		**869.3**		

Table S-4. The rotational constants *A*, *B*, *C* (in MHz) of conformer aaa of ethyl butyrate calculated at different levels of theory and their deviations to the experimental values (calc.–exp.) Δ*A*, Δ*B*, and Δ*C*, respectively (in MHz). The Θ angle (in degree) is also given.

Level of theory	***A***	**Δ*A***	***B***	**Δ*B***	***C***	**Δ*C***	***Θ***
B3LYP/6-31G(d,p)	6308.5	–19.8	799.1	–7.5	725.2	–7.2	0.0
B3LYP/6-31+G(d,p)	6240.4	–87.9	797.0	–9.6	722.6	–9.8	0.0
B3LYP/6-31++G(d,p)	6241.5	–86.8	797.0	–9.6	722.6	–9.8	0.0
B3LYP/6-311G(d,p)	6291.4	–36.9	800.1	–6.5	725.7	–6.7	0.0
B3LYP/6-311+G(d,p)	6258.5	–69.8	798.9	–7.7	724.3	–8.1	0.0
B3LYP/6-311++G(d,p)	6258.8	–69.5	798.9	–7.7	724.3	–8.1	0.0
B3LYP/6-311G(2d,2p)	6364.1	35.8	801.4	–5.2	727.7	–4.7	0.0
B3LYP/6-311+G(2d,2p)	6315.8	–12.5	800.4	–6.2	726.2	–6.2	0.0
B3LYP/6-311++G(2d,2p)	6315.9	–12.4	800.4	–6.2	726.2	–6.2	0.0
B3LYP/6-311G(df,pd)	6304.3	–24.0	802.3	–4.3	727.6	–4.8	0.0
B3LYP/6-311+G(df,pd)	6275.1	–53.2	801.0	–5.6	726.2	–6.2	0.0
B3LYP/6-311++G(df,pd)	6275.4	–52.9	801.0	–5.6	726.2	–6.2	0.0
B3LYP/6-311G(2df,2pd)	6339.8	11.5	802.9	–3.7	728.6	–3.8	0.0
B3LYP/6-311+G(2df,2pd)	6299.5	–28.8	801.8	–4.8	727.1	–5.3	0.0
B3LYP/6-311++G(2df,2pd)	6299.8	–28.5	801.7	–4.9	727.1	–5.3	0.0
B3LYP/6-311G(3df,3pd)	6331.2	2.9	803.2	–3.4	728.7	–3.7	0.0
B3LYP/6-311+G(3df,3pd)	6305.6	–22.7	801.9	–4.7	727.3	–5.1	0.0
B3LYP/6-311++G(3df,3pd)	6305.5	–22.8	801.9	–4.7	727.3	–5.1	0.0
B3LYP/cc-pVDZ	6295.3	–33.0	799.3	–7.3	725.3	–7.1	0.0
B3LYP/aug-cc-pVDZ	6254.7	–73.6	797.6	–9.0	723.3	–9.1	0.0
B3LYP/cc-pVTZ	6304.2	–24.1	802.1	–4.5	727.4	–5.0	0.0
B3LYP/aug-cc-pVTZ	6295.4	–32.9	801.4	–5.2	726.8	–5.6	0.0
B3LYP-D3/6-31G(d,p)	6310.7	–17.6	801.4	–5.2	727.0	–5.4	0.0
B3LYP-D3/6-31+G(d,p)	6246.0	–82.3	799.2	–7.4	724.4	–8.0	0.0
B3LYP-D3/6-31++G(d,p)	6247.1	–81.2	799.2	–7.4	724.4	–8.0	0.0
B3LYP-D3/6-311G(d,p)	6293.7	–34.6	802.4	–4.2	727.6	–4.8	0.0
B3LYP-D3/6-311+G(d,p)	6260.8	–67.5	801.2	–5.4	726.2	–6.2	0.0
B3LYP-D3/6-311++G(d,p)	6261.1	–67.2	801.2	–5.4	726.2	–6.2	0.0
B3LYP-D3/6-311G(2d,2p)	6365.7	37.4	803.6	–3.0	729.5	–2.9	0.0
B3LYP-D3/6-311+G(2d,2p)	6318.7	–9.6	802.7	–3.9	728.1	–4.3	0.0
B3LYP-D3/6-311++G(2d,2p)	6318.8	–9.5	802.7	–3.9	728.1	–4.3	0.0
B3LYP-D3/6-311G(df,pd)	6307.5	–20.8	804.5	–2.1	729.5	–2.9	0.0
B3LYP-D3/6-311+G(df,pd)	6278.3	–50.0	803.3	–3.3	728.2	–4.2	0.0
B3LYP-D3/6-311++G(df,pd)	6278.6	–49.7	803.3	–3.3	728.2	–4.2	0.0
B3LYP-D3/6-311G(2df,2pd)	6342.3	14.0	805.1	–1.5	730.4	–2.0	0.0
B3LYP-D3/6-311+G(2df,2pd)	6303.2	–25.1	804.0	–2.6	729.0	–3.4	0.0
B3LYP-D3/6-311++G(2df,2pd)	6303.6	–24.7	804.0	–2.6	729.0	–3.4	0.0
B3LYP-D3/6-311G(3df,3pd)	6334.1	5.8	805.3	–1.3	730.5	–1.9	0.0
B3LYP-D3/6-311+G(3df,3pd)	6310.0	–18.3	804.1	–2.5	729.2	–3.2	0.0
B3LYP-D3/6-311++G(3df,3pd)	6309.9	–18.4	804.1	–2.5	729.2	–3.2	0.0
B3LYP-D3/cc-pVDZ	6297.1	–31.2	801.6	–5.0	727.2	–5.2	0.0
B3LYP-D3/aug-cc-pVDZ	6259.6	–68.7	799.8	–6.8	725.2	–7.2	0.0
B3LYP-D3/cc-pVTZ	6307.8	–20.5	804.3	–2.3	729.3	–3.1	0.0
B3LYP-D3/aug-cc-pVTZ	6297.8	–30.5	803.9	–2.7	728.8	–3.6	0.0

B3LYP-D3BJ/6-31G(d,p)	6328.3	0.0	802.0	–4.6	727.8	–4.6	0.0
B3LYP-D3BJ/6-31+G(d,p)	6261.6	–66.7	799.9	–6.7	725.2	–7.2	0.0
B3LYP-D3BJ/6-31++G(d,p)	6262.7	–65.6	799.9	–6.7	725.2	–7.2	0.0
B3LYP-D3BJ/6-311G(d,p)	6310.1	–18.2	803.2	–3.4	728.5	–3.9	0.0
B3LYP-D3BJ/6-311+G(d,p)	6279.7	–48.6	801.9	–4.7	727.0	–5.4	0.0
B3LYP-D3BJ/6-311++G(d,p)	6276.4	–51.9	802.0	–4.6	727.1	–5.3	0.0
B3LYP-D3BJ/6-311G(2d,2p)	6384.0	55.7	804.4	–2.2	730.3	–2.1	0.0
B3LYP-D3BJ/6-311+G(2d,2p)	6335.2	6.9	803.4	–3.2	728.9	–3.5	0.0
B3LYP-D3BJ/6-311++G(2d,2p)	6335.3	7.0	803.4	–3.2	728.9	–3.5	0.0
B3LYP-D3BJ/6-311G(df,pd)	6324.0	–4.3	805.2	–1.4	730.3	–2.1	0.0
B3LYP-D3BJ/6-311+G(df,pd)	6296.6	–31.7	803.9	–2.7	728.9	–3.5	0.0
B3LYP-D3BJ/6-311++G(df,pd)	6296.9	–31.4	803.9	–2.7	728.9	–3.5	0.0
B3LYP-D3BJ/6-311G(2df,2pd)	6360.0	31.7	805.8	–0.8	731.2	–1.2	0.0
B3LYP-D3BJ/6-311+G(2df,2pd)	6320.3	–8.0	804.6	–2.0	729.7	–2.7	0.0
B3LYP-D3BJ/6-311++G(2df,2pd)	6320.6	–7.7	804.6	–2.0	729.7	–2.7	0.0
B3LYP-D3BJ/6-311G(3df,3pd)	6351.6	23.3	806.0	–0.6	731.3	–1.1	0.0
B3LYP-D3BJ/6-311+G(3df,3pd)	6326.0	–2.3	804.8	–1.8	730.0	–2.4	0.0
B3LYP-D3BJ/6-311++G(3df,3pd)	6325.9	–2.4	804.8	–1.8	730.0	–2.4	0.0
B3LYP-D3BJ/cc-pVDZ	6314.8	–13.5	802.2	–4.4	728.0	–4.4	0.0
B3LYP-D3BJ/aug-cc-pVDZ	6275.5	–52.8	800.5	–6.1	726.0	–6.4	0.0
B3LYP-D3BJ/cc-pVTZ	6324.0	–4.3	805.1	–1.5	730.1	–2.3	0.0
B3LYP-D3BJ/aug-cc-pVTZ	6315.2	–13.1	804.4	–2.2	729.5	–2.9	0.0
CAM-B3LYP-D3BJ/6-311G(d,p)	6388.3	60.0	809.6	3.0	734.8	2.4	0.0
CAM-B3LYP-D3BJ/6-311+G(d,p)	6353.3	25.0	808.5	1.9	733.4	1.0	0.0
CAM-B3LYP-D3BJ/6-311++G(d,p)	6353.5	25.2	808.5	1.9	733.4	1.0	0.0
CAM-B3LYP-D3BJ/aug-cc-pVDZ[a]	6353.9	25.6	806.9	0.3	732.3	–0.1	0.0
CAM-B3LYP-D3BJ/aug-cc-pVTZ	6391.7	63.4	811.0	4.4	735.9	3.5	0.0
CAM-B3LYP-D3BJ/cc-pVDZ	6399.5	71.2	808.6	2.0	734.3	1.9	0.0
CAM-B3LYP-D3BJ/cc-pVTZ	6401.0	72.7	811.7	5.1	736.6	4.2	0.0
CCSD/cc-pVDZ	6327.8	–0.5	801.2	–5.4	727.5	–4.9	0.0
M06-2X/6-31G(d,p)	6445.8	117.5	808.9	2.3	735.0	2.6	0.0
M06-2X/6-31+G(d,p)	6389.4	61.1	807.4	0.8	733.1	0.7	0.0
M06-2X/6-31++G(d,p)	6389.5	61.2	807.4	0.8	733.1	0.7	0.0
M06-2X/6-311G(d,p)	6430.5	102.2	809.8	3.2	735.6	3.2	0.0
M06-2X/6-311+G(d,p)	6401.6	73.3	809.1	2.5	734.6	2.2	0.0
M06-2X/6-311++G(d,p)	6401.9	73.6	809.1	2.5	734.6	2.2	0.0
M06-2X/6-311G(2d,2p)	6507.6	179.3	810.8	4.2	737.3	4.9	0.0
M06-2X/6-311+G(2d,2p)	6465.3	137.0	810.2	3.6	736.2	3.8	0.0
M06-2X/6-311++G(2d,2p)	6465.4	137.1	810.1	3.5	736.2	3.8	0.0
M06-2X/6-311G(df,pd)	6440.4	112.1	811.4	4.8	736.9	4.5	0.0
M06-2X/6-311+G(df,pd)	6415.1	86.8	810.5	3.9	735.9	3.5	0.0
M06-2X/6-311++G(df,pd)	6415.5	87.2	810.5	3.9	735.9	3.5	0.0
M06-2X/6-311G(2df,2pd)	6480.5	152.2	811.9	5.3	737.8	5.4	0.0
M06-2X/6-311+G(2df,2pd)	6445.6	117.3	811.0	4.4	736.6	4.2	0.0
M06-2X/6-311++G(2df,2pd)	6445.9	117.6	811.0	4.4	736.6	4.2	0.0
M06-2X/6-311G(3df,3pd)	6475.5	147.2	812.1	5.5	737.9	5.5	0.0
M06-2X/6-311+G(3df,3pd)	6454.6	126.3	811.1	4.5	736.8	4.4	0.0
M06-2X/6-311++G(3df,3pd)	6454.6	126.3	811.1	4.5	736.8	4.4	0.0
M06-2X/aug-cc-pVDZ	6419.2	90.9	807.6	1.0	733.8	1.4	0.0

M06-2X/aug-cc-pVTZ	6440.3	112.0	810.9	4.3	736.5	4.1	0.0
M06-2X/cc-pVDZ	6457.4	129.1	809.2	2.6	735.6	3.2	0.0
M06-2X/cc-pVTZ	6446.6	118.3	811.4	4.8	737.0	4.6	0.0
MN15/6-31G(d,p)	6465.5	137.2	807.4	0.8	734.0	1.6	0.0
MN15/6-31+G(d,p)	6394.5	66.2	805.6	–1.0	731.6	–0.8	0.0
MN15/6-31++G(d,p)	6396.0	67.7	805.6	–1.0	731.6	–0.8	0.0
MN15/6-311G(d,p)	6450.3	122.0	810.2	3.6	736.1	3.7	0.0
MN15/6-311+G(d,p)	6419.6	91.3	809.4	2.8	735.0	2.6	0.0
MN15/6-311++G(d,p)	6419.8	91.5	809.4	2.8	735.1	2.7	0.0
MN15/6-311G(2d,2p)	6547.9	219.6	811.8	5.2	738.6	6.2	0.0
MN15/6-311+G(2d,2p)	6500.8	172.5	811.0	4.4	737.3	4.9	0.0
MN15/6-311++G(2d,2p)	6500.3	172.0	811.0	4.4	737.3	4.9	0.0
MN15/6-311G(df,pd)	6468.5	140.2	812.3	5.7	738.0	5.6	0.0
MN15/6-311+G(df,pd)	6443.2	114.9	811.2	4.6	736.8	4.4	0.0
MN15/6-311++G(df,pd)	6443.2	114.9	811.2	4.6	736.8	4.4	0.0
MN15/6-311G(2df,2pd)	6525.9	197.6	813.0	6.4	739.3	6.9	0.0
MN15/6-311+G(2df,2pd)	6488.0	159.7	812.0	5.4	738.0	5.6	0.0
MN15/6-311++G(2df,2pd)	6488.1	159.8	812.0	5.4	738.0	5.6	0.0
MN15/6-311G(3df,3pd)	6508.8	180.5	813.2	6.6	739.2	6.8	0.0
MN15/6-311+G(3df,3pd)	6485.3	157.0	812.0	5.4	738.0	5.6	0.0
MN15/6-311++G(3df,3pd)	6485.8	157.5	812.0	5.4	738.0	5.6	0.0
MN15/cc-pVDZ	6483.6	155.3	808.1	1.5	735.0	2.6	0.0
MN15/aug-cc-pVDZ	6433.8	105.5	807.7	1.1	734.0	1.6	0.0
MN15/cc-pVTZ	6481.5	153.2	812.5	5.9	738.3	5.9	0.0
MN15/aug-cc-pVTZ	6482.0	153.7	812.6	6.0	738.4	6.0	0.0
PBE0/6-31G(d,p)	6276.4	–51.9	795.4	–11.2	721.9	–10.5	0.0
PBE0/6-31+G(d,p)	6202.8	–125.5	793.2	–13.4	719.1	–13.3	0.0
PBE0/6-31++G(d,p)	6203.9	–124.4	793.2	–13.4	719.1	–13.3	0.0
PBE0/6-311G(d,p)	6263.1	–65.2	796.6	–10.0	722.7	–9.7	0.0
PBE0/6-311+G(d,p)	6225.7	–102.6	795.3	–11.3	721.1	–11.3	0.0
PBE0/6-311++G(d,p)	6226.3	–102.0	795.3	–11.3	721.1	–11.3	0.0
PBE0/6-311G(2d,2p)	6333.6	5.3	797.6	–9.0	724.4	–8.0	0.0
PBE0/6-311+G(2d,2p)	6279.4	–48.9	796.6	–10.0	722.8	–9.6	0.0
PBE0/6-311++G(2d,2p)	6279.5	–48.8	796.5	–10.1	722.8	–9.6	0.0
PBE0/6-311G(df,pd)	6276.9	–51.4	798.7	–7.9	724.6	–7.8	0.0
PBE0/6-311+G(df,pd)	6243.8	–84.5	797.2	–9.4	722.9	–9.5	0.0
PBE0/6-311++G(df,pd)	6244.4	–83.9	797.2	–9.4	722.9	–9.5	0.0
PBE0/6-311G(2df,2pd)	6312.8	–15.5	799.2	–7.4	725.4	–7.0	0.0
PBE0/6-311+G(2df,2pd)	6266.8	–61.5	797.9	–8.7	723.7	–8.7	0.0
PBE0/6-311++G(2df,2pd)	6267.2	–61.1	797.9	–8.7	723.7	–8.7	0.0
PBE0/6-311G(3df,3pd)	6302.7	–25.6	799.5	–7.1	725.5	–6.9	0.0
PBE0/6-311+G(3df,3pd)	6273.0	–55.3	798.1	–8.5	723.9	–8.5	0.0
PBE0/6-311++G(3df,3pd)	6272.8	–55.5	798.1	–8.5	723.9	–8.5	0.0
PBE0/cc-pVDZ	6261.3	–67.0	795.9	–10.7	722.2	–10.2	0.0
PBE0/aug-cc-pVDZ	6218.8	–109.5	793.9	–12.7	720.0	–12.4	0.0
PBE0/cc-pVTZ	6271.8	–56.5	798.3	–8.3	724.1	–8.3	0.0
PBE0/aug-cc-pVTZ	6259.1	–69.2	797.5	–9.1	723.3	–9.1	0.0
PBE0-D3/6-31G(d,p)	6267.7	–60.6	796.5	–10.1	722.7	–9.7	0.0

PBE0-D3/6-31+G(d,p)	6195.6	–132.7	794.3	–12.3	719.9	–12.5	0.0
PBE0-D3/6-31++G(d,p)	6196.7	–131.6	794.2	–12.4	719.9	–12.5	0.0
PBE0-D3/6-311G(d,p)	6254.7	–73.6	797.7	–8.9	723.4	–9.0	0.0
PBE0-D3/6-311+G(d,p)	6218.3	–110.0	796.4	–10.2	721.9	–10.5	0.0
PBE0-D3/6-311++G(d,p)	6218.9	–109.4	796.4	–10.2	721.9	–10.5	0.0
PBE0-D3/6-311G(2d,2p)	6324.5	–3.8	798.7	–7.9	725.1	–7.3	0.0
PBE0-D3/6-311+G(2d,2p)	6271.3	–57.0	797.6	–9.0	723.5	–8.9	0.0
PBE0-D3/6-311++G(2d,2p)	6271.4	–56.9	797.6	–9.0	723.5	–8.9	0.0
PBE0-D3/6-311G(df,pd)	6268.4	–59.9	799.8	–6.8	725.3	–7.1	0.0
PBE0-D3/6-311+G(df,pd)	6236.2	–92.1	798.3	–8.3	723.7	–8.7	0.0
PBE0-D3/6-311++G(df,pd)	6236.8	–91.5	798.3	–8.3	723.7	–8.7	0.0
PBE0-D3/6-311G(2df,2pd)	6303.9	–24.4	800.2	–6.4	726.1	–6.3	0.0
PBE0-D3/6-311+G(2df,2pd)	6258.8	–69.5	798.9	–7.7	724.5	–7.9	0.0
PBE0-D3/6-311++G(2df,2pd)	6259.2	–69.1	798.9	–7.7	724.4	–8.0	0.0
PBE0-D3/6-311G(3df,3pd)	6294.0	–34.3	800.5	–6.1	726.2	–6.2	0.0
PBE0-D3/6-311+G(3df,3pd)	6265.0	–63.3	799.1	–7.5	724.7	–7.7	0.0
PBE0-D3/6-311++G(3df,3pd)	6264.9	–63.4	799.1	–7.5	724.7	–7.7	0.0
PBE0-D3/cc-pVDZ	6252.4	–75.9	797.0	–9.6	723.0	–9.4	0.0
PBE0-D3/aug-cc-pVDZ	6211.3	–117.0	795.0	–11.6	720.8	–11.6	0.0
PBE0-D3/cc-pVTZ	6263.7	–64.6	799.3	–7.3	724.8	–7.6	0.0
PBE0-D3/aug-cc-pVTZ	6251.3	–77.0	798.6	–8.0	724.1	–8.3	0.0
ωB97X-D/6-31G(d,p)	6357.0	28.7	807.1	0.5	732.4	0.0	0.0
ωB97X-D/6-31+G(d,p)	6302.3	–26.0	805.8	–0.8	730.6	–1.8	0.0
ωB97X-D/6-31++G(d,p)	6302.4	–25.9	805.8	–0.8	730.6	–1.8	0.0
ωB97X-D/6-311G(d,p)	6317.2	–11.1	807.7	1.1	732.3	–0.1	0.0
ωB97X-D/6-311+G(d,p)	6317.5	–10.8	807.7	1.1	732.3	–0.1	0.0
ωB97X-D/6-311++G(d,p)	6347.0	18.7	808.5	1.9	733.4	1.0	0.0
ωB97X-D/6-311G(2d,2p)	6415.4	87.1	809.6	3.0	735.1	2.7	0.0
ωB97X-D/6-311+G(2d,2p)	6372.3	44.0	808.9	2.3	734.0	1.6	0.0
ωB97X-D/6-311++G(2d,2p)	6372.5	44.2	808.9	2.3	733.9	1.5	0.0
ωB97X-D/6-311G(df,pd)	6356.8	28.5	810.4	3.8	735.1	2.7	0.0
ωB97X-D/6-311+G(df,pd)	6331.0	2.7	809.5	2.9	734.0	1.6	0.0
ωB97X-D/6-311++G(df,pd)	6331.2	2.9	809.5	2.9	734.0	1.6	0.0
ωB97X-D/6-311G(2df,2pd)	6389.3	61.0	810.9	4.3	735.8	3.4	0.0
ωB97X-D/6-311+G(2df,2pd)	6353.4	25.1	810.1	3.5	734.6	2.2	0.0
ωB97X-D/6-311++G(2df,2pd)	6353.8	25.5	810.0	3.4	734.6	2.2	0.0
ωB97X-D/6-311G(3df,3pd)	6381.3	53.0	811.2	4.6	736.0	3.6	0.0
ωB97X-D/6-311+G(3df,3pd)	6360.3	32.0	810.3	3.7	734.9	2.5	0.0
ωB97X-D/6-311++G(3df,3pd)	6360.1	31.8	810.3	3.7	734.9	2.5	0.0
ωB97X-D/aug-cc-pVDZ	6317.9	–10.4	805.6	–1.0	730.8	–1.6	0.0
ωB97X-D/aug-cc-pVTZ	6349.4	21.1	809.9	3.3	734.5	2.1	0.0
ωB97X-D/cc-pVDZ	6351.9	23.6	806.9	0.3	732.3	–0.1	0.0
ωB97X-D/cc-pVTZ	6356.1	27.8	810.4	3.8	734.9	2.5	0.0
MP2/6-31G(d,p)	6345.4	17.1	807.6	1.0	732.6	0.2	0.0
MP2/6-31+G(d,p)	6282.5	–45.8	805.5	–1.1	730.0	–2.4	0.0
MP2/6-31++G(d,p)	6279.8	–48.5	805.6	–1.0	730.1	–2.3	0.0
MP2/6-311G(d,p)	6356.6	28.3	807.6	1.0	732.9	0.5	0.0

MP2/6-311+G(d,p)	6332.9	4.6	806.3	–0.3	731.4	–1.0	0.0
MP2/6-311++G(d,p)	6332.9	4.6	806.3	–0.3	731.4	–1.0	0.0
MP2/6-311G(2d,2p)	6427.9	99.6	809.6	3.0	735.2	2.8	0.0
MP2/6-311+G(2d,2p)	6379.3	51.0	808.4	1.8	733.6	1.2	0.0
MP2/6-311++G(2d,2p)	6379.7	51.4	808.4	1.8	733.6	1.2	0.0
MP2/6-311G(df,pd)	6421.3	93.0	813.2	6.6	738.2	5.8	0.0
MP2/6-311+G(df,pd)	6399.5	71.2	811.3	4.7	736.4	4.0	0.0
MP2/6-311++G(df,pd)	6401.9	73.6	811.2	4.6	736.4	4.0	0.0
MP2/6-311G(2df,2pd)	6427.8	99.5	814.6	8.0	739.4	7.0	0.0
MP2/6-311+G(2df,2pd)	6390.9	62.6	813.1	6.5	737.6	5.2	0.0
MP2/6-311++G(2df,2pd)	6391.2	62.9	813.1	6.5	737.6	5.2	0.0
MP2/6-311G(3df,3pd)	6409.2	80.9	814.2	7.6	738.8	6.4	0.0
MP2/6-311+G(3df,3pd)	6384.9	56.6	812.6	6.0	737.2	4.8	0.0
MP2/6-311++G(3df,3pd)	6385.3	57.0	812.6	6.0	737.2	4.8	0.0
MP2/aug-cc-pVDZ	6285.6	–42.7	800.2	–6.4	726.0	–6.4	0.0
MP2/aug-cc-pVTZ	6371.2	42.9	811.4	4.8	736.1	3.7	0.0
MP2/cc-pVDZ	6329.5	1.2	804.2	–2.4	729.9	–2.5	0.0
MP2/cc-pVTZ	6386.3	58.0	812.3	5.7	737.0	4.6	0.0
Expt.	**6328.3**		**806.6**		**732.4**		

Table S-5. Observed 172 frequencies ($\nu_{Obs.}$) of conformer Maa of ethyl butyrate. $\nu_{Obs.} - \nu_{Calc.}$ values as obtained with the program *XIAM*.

J	*K*a	*K*c	*J*	*K*a	*K*c	$\nu_{Obs.}$	$\nu_{Obs.} - \nu_{Calc.}$
upper level			lower level			MHz	kHz
2	1	1	1	0	1	7949.384	–1.1
2	2	1	1	1	0	16582.677	–3.7
2	2	0	2	1	1	13002.318	0.1
2	2	1	2	1	2	13105.601	–1.2
3	0	3	2	0	2	5318.239	0.4
3	1	2	2	1	1	5370.710	–2.2
3	1	3	2	1	2	5267.219	2.9
3	2	2	2	1	1	18321.301	–4.2
3	2	2	2	1	2	18424.774	–20.5
3	2	1	2	2	0	5320.002	–10.6
3	2	2	2	2	1	5319.192	–0.4
3	2	1	3	1	2	12951.624	5.7
3	2	2	3	1	2	12950.600	7.0
4	0	4	3	0	3	7090.001	–0.3
4	1	3	3	0	3	11616.711	8.1
4	1	3	3	1	2	7160.688	–0.3
4	1	4	3	1	3	7022.685	0.1
4	2	2	3	2	1	7094.121	–0.1
4	2	3	3	2	2	7092.072	1.4
4	3	2	3	3	1	7092.867	6.9
4	2	2	4	1	3	12885.052	0.4
4	2	3	4	1	3	12881.978	2.2
4	2	3	4	1	4	13226.970	5.8
5	0	5	4	0	4	8860.921	–0.5
5	1	5	4	0	4	12959.635	–2.8
5	1	4	4	1	3	8950.436	–0.7
5	1	5	4	1	4	8777.925	0.5
5	2	4	4	1	3	21746.765	–0.2
5	2	3	4	1	4	22098.939	9.3
5	2	3	4	2	2	8868.889	–0.7
5	2	4	4	2	3	8864.790	0.6
5	3	2	4	3	1	8866.227	–8.9
5	3	3	4	3	2	8866.227	7.1
5	4	1	4	4	0	8866.369	1.7
5	2	3	5	1	4	12803.506	1.4
5	2	4	5	1	4	12796.330	1.5
5	2	4	5	1	5	13313.829	0.0
5	3	2	5	2	3	21748.743	13.0
5	3	3	5	2	4	21755.882	–2.8
6	0	6	5	0	5	10630.791	0.3
6	1	5	5	0	5	15356.118	2.0
6	1	5	5	1	4	10739.898	–1.2

6	1	6	5	1	5	10532.880	–0.5
6	2	4	5	2	3	10644.481	–0.5
6	2	5	5	2	4	10637.309	0.1
6	3	3	5	2	4	32395.622	1.1
6	5	1	5	5	0	10640.148	4.0
5	3	2	6	2	4	11104.235	–13.5
6	2	4	6	1	5	12708.088	1.1
6	2	5	6	1	6	13418.264	6.6
6	3	3	6	2	4	21743.968	4.7
6	3	4	6	2	5	21758.248	0.0
7	0	7	6	0	6	12399.403	0.1
7	1	6	6	1	5	12529.013	–0.5
7	1	7	6	1	6	12287.500	0.1
7	2	5	6	2	4	12421.056	–0.5
7	2	6	6	2	5	12409.588	–1.1
7	3	5	6	2	4	34157.129	–1.5
7	3	4	6	2	5	34171.642	2.7
7	3	4	6	3	3	12413.326	–1.3
7	3	5	6	3	4	12413.228	–3.3
7	4	3	6	4	2	12413.138	–1.0
7	5	2	6	5	1	12413.546	0.8
7	5	3	6	5	2	12413.546	0.8
7	6	1	6	6	0	12414.241	–5.8
7	2	6	7	1	7	13540.349	2.4
7	3	4	7	2	5	21736.237	3.0
7	3	5	7	2	6	21761.891	0.8
8	0	8	7	0	7	14166.557	–0.2
8	0	8	7	1	7	10277.654	–0.2
8	1	7	7	1	6	14317.714	–1.5
8	1	8	7	1	7	14041.732	–0.1
8	2	6	7	1	7	27764.936	3.2
8	2	6	7	2	5	14198.769	–1.0
8	2	7	7	2	6	14181.589	–1.0
8	3	6	7	2	5	35922.979	–4.5
8	3	5	7	2	6	35949.153	1.1
8	3	5	7	3	4	14187.101	–0.6
8	3	6	7	3	5	14186.908	–1.6
8	4	4	7	4	3	14186.605	–0.5
8	5	3	7	5	2	14186.967	0.2
8	5	4	7	5	3	14186.967	0.2
8	6	2	7	6	1	14187.719	4.2
8	7	2	7	7	1	14188.741	6.7
8	2	6	8	1	7	12481.187	2.6
8	2	7	8	1	8	13680.206	1.5
8	3	5	8	2	6	21724.571	5.3
8	3	6	8	2	7	21767.213	3.2
9	0	9	8	0	8	15932.060	–0.5

9	0	9	8	1	8	12167.980	–2.5
9	1	8	8	1	7	16105.937	–1.1
9	1	9	8	1	8	15795.529	0.1
9	2	8	8	1	7	28391.457	–2.8
9	2	7	8	2	6	15977.768	–0.7
9	2	8	8	2	7	15953.269	–2.6
9	3	6	8	3	5	15961.066	–2.9
9	3	7	8	3	6	15960.717	0.2
9	4	5	8	4	4	15960.135	–1.7
9	4	6	8	4	5	15960.135	0.1
9	5	4	8	5	3	15960.412	0.4
9	5	5	8	5	4	15960.412	0.4
9	6	3	8	6	2	15961.187	2.6
9	7	2	8	7	1	15962.297	6.1
9	2	7	9	1	8	12353.016	0.9
9	2	8	9	1	9	13837.947	–0.1
9	3	7	9	2	8	21774.654	–1.0
10	0	10	9	0	9	17695.731	–0.5
10	1	9	9	1	8	17893.610	–1.0
10	1	10	9	1	9	17548.843	–1.9
10	2	8	9	2	7	17758.188	0.0
10	2	9	9	2	8	17724.593	–0.9
10	3	7	9	3	6	17735.260	–3.4
10	3	8	9	3	7	17734.657	–2.8
10	6	4	9	6	3	17734.657	1.0
10	6	5	9	6	4	17734.657	1.0
10	7	3	9	7	2	17735.841	6.0
10	7	4	9	7	3	17735.841	6.0
10	2	8	10	1	9	12217.592	–0.1
10	2	9	10	1	10	14013.693	–3.2
10	3	8	10	2	9	21784.720	–0.9
11	0	11	10	0	10	19457.405	0.0
11	1	10	10	1	9	19680.660	0.0
11	1	11	10	1	10	19301.637	–0.5
11	2	9	10	1	9	31757.739	0.5
11	2	10	10	1	10	33509.221	8.0
11	2	9	10	2	8	19540.147	0.5
11	2	10	10	2	9	19495.516	–0.9
11	2	9	11	1	10	12077.079	0.5
11	2	10	11	1	11	14207.567	–8.5
12	0	12	11	0	11	21216.936	–1.0
12	1	11	11	1	10	21467.006	–0.9
12	1	12	11	1	11	21053.867	–0.8
12	2	10	11	1	10	33400.819	–0.8
12	2	10	11	2	9	21323.738	–3.3
12	2	11	11	2	10	21265.998	–2.6
12	2	10	12	1	11	11933.815	2.1

12	2	11	12	1	12	14419.700	–8.4
12	3	10	12	2	11	21814.911	–0.3
13	0	13	12	0	12	22974.209	–1.4
13	1	12	12	1	11	23252.568	–0.8
13	1	13	12	1	12	22805.501	1.0
13	1	12	12	2	11	11522.222	8.3
13	2	11	12	2	10	23109.038	–4.3
13	2	12	12	2	11	23036.001	–4.2
13	2	11	13	1	12	11790.287	0.6
13	2	12	13	1	13	14650.210	–3.6
13	3	11	13	2	12	21836.232	0.9
14	1	14	13	0	13	27549.611	–3.9
14	2	12	14	1	13	11649.118	2.5
14	3	12	14	2	13	21862.553	–1.6
15	2	13	14	2	12	26684.873	–1.5
15	2	13	15	1	14	11513.011	1.7
15	3	13	15	2	14	21894.559	–0.1
16	0	16	15	0	15	28231.818	0.3
16	1	15	15	1	14	28603.639	0.3
16	2	14	15	2	13	28475.369	6.1
16	2	15	15	2	14	28342.745	–3.4
16	2	14	16	1	15	11384.734	0.5
16	3	14	16	2	15	21932.949	3.2
17	0	17	16	0	16	29979.593	–1.0
17	0	17	16	1	16	27509.266	7.1
17	2	15	16	2	14	30267.465	–1.5
17	2	16	16	2	15	30110.439	–3.0
17	2	15	17	1	16	11267.071	–2.1
17	3	15	17	2	16	21978.430	–5.6
18	2	16	18	1	17	11162.794	0.2
18	3	16	18	2	17	22031.763	–1.1
19	2	17	19	1	18	11074.608	1.0
19	3	17	19	2	18	22093.671	–6.3
20	2	18	20	1	19	11005.136	–2.5
21	2	19	21	1	20	10956.904	–0.2
24	2	22	24	1	23	10962.807	1.6

Table S-6. Observed 117 frequencies ($\nu_{Obs.}$) of conformer aaa of ethyl butyrate. $\nu_{Obs.} - \nu_{Calc.}$ values as obtained with the program *XIAM*.

J	*K*a	*K*c	*J*	*K*a	*K*c	$\nu_{Obs.}$	$\nu_{Obs.} - \nu_{Calc.}$
upper level			lower level			MHz	kHz
2	2	0	2	1	1	16565.566	1.5
3	1	3	2	0	2	9953.295	–3.6
3	2	1	3	1	2	16457.671	–3.2
3	2	2	3	1	3	16899.294	6.7
3	2	2	4	1	3	10151.151	–5.4
4	1	3	4	0	4	5939.084	5.4
4	2	2	4	1	3	16317.581	–4.4
4	2	3	4	1	4	17048.640	9.5
5	0	5	4	0	4	7679.976	1.1
5	1	5	4	0	4	12702.953	1.9
5	1	4	4	1	3	7877.074	1.1
5	1	5	4	1	4	7506.056	–5.6
5	1	4	5	0	5	6136.178	1.4
5	2	3	5	1	4	16148.523	–5.4
5	2	4	5	1	5	17235.748	5.7
5	3	2	5	2	3	27773.730	4.6
6	0	6	5	0	5	9207.845	1.1
6	1	6	5	0	5	14028.267	–5.5
6	1	5	5	1	4	9450.365	0.0
6	1	6	5	1	5	9005.296	–0.3
6	1	5	6	0	6	6378.702	4.4
6	2	5	6	1	6	17460.890	4.0
6	3	3	6	2	4	27755.370	0.2
7	0	7	6	0	6	10731.353	1.3
7	1	7	6	0	6	15323.921	–1.2
7	1	6	6	1	5	11022.457	0.6
7	1	7	6	1	6	10503.496	2.3
7	2	5	6	2	4	10808.339	1.8
7	2	6	6	2	5	10766.963	2.1
7	1	6	7	0	7	6669.805	2.7
7	2	5	7	1	6	15740.416	0.8
7	2	6	7	1	7	17724.352	–1.2
7	3	4	7	2	5	27726.263	1.9
7	3	5	7	2	6	27818.583	4.5
8	0	8	7	0	7	12249.869	1.5
8	1	7	7	1	6	12593.111	0.1
8	1	8	7	1	7	12000.517	2.0
8	2	7	7	1	6	27949.729	–4.8
8	2	6	7	2	5	12364.420	0.4
8	2	7	7	2	6	12302.614	1.6
7	3	5	8	2	6	15360.870	4.8
7	3	4	8	2	7	15516.945	2.5

8	1	7	8	0	8	7013.051	5.3
8	2	6	8	1	7	15511.720	–3.9
8	2	7	8	1	8	18026.449	–1.6
8	3	5	8	2	6	27683.065	3.0
8	3	6	8	2	7	27836.001	–14.8
9	0	9	8	0	8	13762.842	1.3
9	1	9	8	1	8	13496.238	1.8
9	2	8	8	2	7	13837.273	1.7
9	3	6	8	3	5	13864.150	–0.3
8	3	6	9	2	7	13755.878	5.1
9	1	8	9	0	9	7412.282	1.6
9	2	7	9	1	8	15274.689	–1.4
9	2	8	9	1	9	18367.480	–5.8
9	3	6	9	2	7	27622.170	–0.2
9	3	7	9	2	8	27860.737	–13.5
10	0	10	9	0	9	15269.835	2.0
10	0	10	9	1	9	11193.221	1.5
10	1	10	9	1	9	14990.551	1.2
10	2	9	9	2	8	15370.817	1.4
10	3	8	9	3	7	15404.526	0.9
9	3	6	10	2	9	12494.224	–2.2
10	1	9	10	0	10	7871.523	–2.2
10	2	8	10	1	9	15036.130	2.3
10	2	9	10	1	10	18747.751	–0.5
10	3	7	10	2	8	27539.852	0.6
10	3	8	10	2	9	27894.457	–2.9
11	0	11	10	0	10	16770.552	1.2
11	0	11	10	1	10	12973.219	–1.6
11	1	10	10	1	9	17293.824	0.2
11	1	11	10	1	10	16483.367	0.7
11	2	9	10	2	8	17061.003	0.1
11	2	10	10	2	9	16903.125	0.8
10	3	8	11	2	9	10470.893	7.0
10	3	7	11	2	10	10999.295	–3.3
11	1	10	11	0	11	8394.795	–3.1
11	2	9	11	1	10	14803.311	4.2
11	2	10	11	1	11	19167.510	0.6
11	3	8	11	2	9	27432.403	–3.8
11	3	9	11	2	10	27938.943	4.5
12	0	12	11	0	11	18264.876	1.1
12	0	12	11	1	11	14754.727	–2.1
12	1	11	11	1	10	18855.995	–1.5
12	1	12	11	1	11	17974.614	–0.7
12	2	10	11	2	9	18636.493	–0.1
12	2	11	11	2	10	18434.076	–1.6
12	1	11	12	0	12	8985.926	6.3
12	2	10	12	1	11	14583.803	–0.4

12	2	11	12	1	12	19626.966	–6.4
12	3	9	12	2	10	27296.373	0.1
12	3	10	12	2	11	27996.070	–7.0
13	1	12	12	1	11	20415.255	1.6
13	2	11	12	2	10	20216.773	–2.4
13	2	12	12	2	11	19963.562	3.1
13	2	11	13	1	12	14385.324	–1.5
13	2	12	13	1	13	20126.287	–0.9
13	3	10	13	2	11	27128.750	5.6
13	3	11	13	2	12	28067.841	0.0
14	1	13	14	0	14	10384.679	2.9
14	2	12	14	1	13	14215.533	–1.0
14	2	13	14	1	14	20665.520	–1.3
14	3	11	14	2	12	26927.212	8.6
14	3	12	14	2	13	28156.249	0.4
15	2	13	15	1	14	14081.881	5.5
15	3	12	15	2	13	26690.337	0.2
15	3	13	15	2	14	28263.344	–4.1
16	2	14	16	1	15	13991.440	–1.9
17	2	15	17	1	16	13950.867	–4.0
18	2	16	18	1	17	13966.289	–4.8
19	2	17	19	1	18	14043.325	–0.2
20	2	18	20	1	19	14187.100	14.0
21	2	19	21	1	20	14402.242	1.0
22	2	20	22	1	21	14693.027	–6.5
23	2	21	23	1	22	15063.301	0.2
24	2	22	24	1	23	15516.457	–0.8
25	2	23	25	1	24	16055.446	2.0

Table S-7. Overview of different carbonyl compounds investigated to probe for the sensitivity of the dihedral predictions at different levels of theory (see Figure 5 and text). Molecules are numbered according to Figure 5.

			MP2/6–311++Gdp				**MP2/cc–pVDZ**				**B3LYP–D3BJ/cc–pVDZ**		
	Θ		**Exp.**	**Calc.**	**%**	**Θ**	**Exp.**	**Calc.**	**%**	**Θ**	**Exp.**	**Calc.**	**%**
(**1**)	33.7	*A*	6059.3	5520.6	8.9	15.9	6059.3	6046.6	0.2	13.3	6059.3	6168.8	–1.8
		B	1421.3	1451.6	–2.1		1421.3	1428.7	–0.5		1421.3	1413.0	0.6
		C	1333.3	1414.3	–6.1		1333.3	1327.7	0.4		1333.3	1309.4	1.8
(**2**)	33.5	*A*	5063.2	4407.0	13.0	14	5063.2	5060.9	0.0	12.1	5063.2	5204.8	–2.8
		B	897.7	932.3	–3.9		897.7	900.9	–0.4		897.7	890.0	0.9
		C	846.4	897.4	–6.0		846.4	844.0	0.3		846.4	832.1	1.7
(**3**)	34.7	*A*	3599.0	3101.3	13.8	15.1	3599.0	3598.9	0.0	12	3599.0	3711.7	–3.1
		B	625.4	664.2	–6.2		625.4	626.6	–0.2		625.4	617.3	1.3
		C	585.8	616.4	–5.2		585.8	584.6	0.2		585.8	576.5	1.6
(**4**)	34.7	*A*	5238.1	4571.6	12.7	16.2	5238.1	5259.6	–0.4	13.6	5238.1	5366.4	–2.4
		B	903.8	941.4	–4.2		903.8	904.4	–0.1		903.8	895.2	0.9
		C	869.3	916.5	–5.4		869.3	865.6	0.4		869.3	854.4	1.7
(**5**)	36.8	*A*	4437.2	3509.1	20.9	15.4	4437.2	4471.3	–0.8	12.4	4437.2	4618.4	–4.1
		B	612.2	653.7	–6.8		612.2	612.6	–0.1		612.2	605.5	1.1
		C	595.8	639.1	–7.3		595.8	592.8	0.5		595.8	584.4	1.9
(**6**)	59	*A*	4013.5	3378.5	15.8	17.8	4013.5	4040.7	–0.7	15.3	4013.5	4052.2	–1.0
		B	681.6	751.3	–10.2		681.6	680.6	0.1		681.6	677.5	0.6
		C	649.3	708.1	–9.1		649.3	644.0	0.8		649.3	638.4	1.7
(**11**)	52	*A*	2604.5	2480.4	4.8	25.5	2604.5	2745.3	–5.4	22.5	2604.5	2775.2	–6.6
		B	885.4	913.5	–3.2		885.4	871.5	1.6		885.4	865.4	2.3
		C	795	813.2	–2.3		795	772.5	2.8		795	764.1	3.9
(**12**)	58.5	*A*	2007.2	1680.9	16.3	25.3	2007.2	2253.7	–12.3	21.5	2007.2	2315.7	–15.4
		B	654.1	734.0	–12.2		654.1	621.4	5.0		654.1	613.3	6.2
		C	566.4	593.6	–4.8		566.4	547.7	3.3		566.4	541.0	4.5
(**7**)	19.2	*A*	6554.0	6480.0	1.1	11.2	6554.0	6301.0	3.9	11.5	6554.0	6546.8	0.1
		B	2148.0	2156.0	–0.4		2148.0	2169.0	–1.0		2148.0	2140.8	0.3
		C	1927.0	1925.0	0.1		1927.0	1975.0	–2.5		1927.0	1914.5	0.6
(**8**)	19.4	*A*	5864.8	5573.0	5.0	11.7	5864.8	5801.0	1.1	11	5864.8	5864.6	0.0
		B	1244.4	1259.0	–1.2		1244.4	1248.0	–0.3		1244.4	1239.5	0.4
		C	1153.4	1181.0	–2.4		1153.4	1154.0	–0.1		1153.4	1147.1	0.5
(**9**)	19	*A*	4465.2	4217.0	5.6	11.6	4465.2	4409.0	1.3	11.0	4465.2	4465.3	0.0
		B	808.2	822.0	–1.7		808.2	811.0	–0.3		808.2	804.8	0.4
		C	766.2	784.0	–2.3		766.2	767.0	–0.1		766.2	761.5	0.6
(**10**)	18.9	*A*	4184.0	3962.0	5.3	11.6	4184.0	4139.0	1.1	11.0	4184.0	4183.0	0.0
		B	528.0	536.0	–1.5		528.0	529.0	–0.2		528.0	526.0	0.4
		C	508.0	517.0	–1.8		508.0	508.0	0.0		508.0	505.0	0.6
(**14**)	7.7	*A*	4336.7	4305.9	0.7	4.0	4336.7	4291.4	1.0	2.7	4336.7	4313.6	0.5
		B	473.9	475.7	–0.4		473.9	475.1	–0.3		473.9	472.9	0.2
		C	450.0	451.9	–0.4		450.0	450.1	0.0		450.0	447.9	0.5

(**13**)	–	*A*	1525.3	1527.5	–0.1	–	1525.3	1517.7	0.5	–	1525.3	1509.4	1.0
		B	894.2	897.6	–0.4		894.2	893.7	0.1		894.2	886.3	0.9
		C	675.5	679.2	–0.5		675.5	677.4	–0.3		675.5	673.0	0.4

Table S-7. Continued.

			B3LYP/cc-pVDZ				B3LYP-D3BJ/6-311++G(d.p)		
	Θ		**Exp.**	**Calc.**	**%**	**Θ**	**Exp.**	**Calc.**	**%**
(**1**)	12.0	*A*	6059.3	6222.8	–2.7	23.1	6059.3	5908.0	2.5
		B	1421.3	1397.5	1.7		1421.3	1413.0	0.6
		C	1333.3	1293.8	3.0		1333.3	1341.5	–0.6
(**2**)	11.2	*A*	5063.2	5276.3	–4.2	22.9	5063.2	4890.1	3.4
		B	897.7	877.4	2.3		897.7	894.8	0.3
		C	846.4	821.6	2.9		846.4	851.2	–0.6
(**3**)	11.1	*A*	3599.0	3786.5	–5.2	23	3599.0	3461.6	3.8
		B	625.4	606.1	3.1		625.4	626.2	–0.1
		C	585.8	568.1	3.0		585.8	587.7	–0.3
(**4**)	12.6	*A*	5238.1	5404.6	–3.2	23.5	5238.1	5010.8	4.3
		B	903.8	886.9	1.9		903.8	903.6	0.0
		C	869.3	845.4	2.7		869.3	874.5	–0.6
(**5**)	13.9	*A*	4013.5	4047.0	–0.8	17.8	4013.5	3892	3.0
		B	681.6	673.0	1.3		681.6	679.4	0.3
		C	649.3	633.1	2.5		649.3	657.1	–1.2
(**6**)	11.5	*A*	4437.2	4686.3	–5.6	23.4	4437.2	4148	6.5
		B	612.2	598.1	2.3		612.2	612.8	–0.1
		C	595.8	577.3	3.1		595.8	603.2	–1.2
(**11**)	23.1	*A*	2604.5	2756.6	–5.8	44.8	2604.5	2530.2	2.9
		B	885.4	859.0	3.0		885.4	885.6	0.0
		C	795.0	760.5	4.3		795	797.0	–0.3
(**12**)	22.1	*A*	2007.2	2297.8	–14.5	47	2007.2	1866.3	7.0
		B	654.1	608.5	7.0		654.1	670.6	–2.5
		C	566.4	538.0	5.0		566.4	571.6	–0.9
(**7**)	10.6	*A*	6554.0	6590	–0.5	15.7	6554.0	6453.4	1.5
		B	2148.0	2115	1.5		2148.0	2137.4	0.5
		C	1927.0	1892	1.8		1927.0	1933.5	–0.3
(**8**)	10.3	*A*	5864.8	5914	–0.8	15.3	5864.8	5759.5	1.8
		B	1244.4	1223	1.7		1244.4	1237.9	0.5
		C	1153.4	1133	1.8		1153.4	1155	–0.1
(**9**)	10.0	*A*	4465.2	4535.0	–1.6	15.7	4465.2	4365.0	2.2
		B	808.2	791.0	2.1		808.2	805.0	0.4
		C	766.2	750.0	2.1		766.2	767.0	–0.1
(**10**)	10.0	*A*	4184.0	4236.0	–1.2	15.6	4184.0	4097.0	2.1
		B	528.0	518.0	1.9		528.0	526.0	0.4
		C	508.0	498.0	2.0		508.0	507.0	0.2

(**14**)	2.7	*A*	4336.7	4338.1	0.0	6.1	4336.7	4340.4	–0.1
		B	473.9	467.1	1.4		473.9	469.7	0.9
		C	450.0	443.1	1.5		450.0	446.0	0.9
(**13**)	–	*A*	1525.3	1495.7	1.9	–	1525.3	1511.0	0.9
		B	894.2	875.1	2.1		894.2	886.0	0.9
		C	675.5	665.8	1.4		675.5	671.6	0.6

Table S-8. The rotational constants *A*, *B*, *C* (in MHz) of the C_1 conformer of ethyl 2-methylbutyrate calculated at different levels of theory and their deviations to the experimental values (calc.–exp.) Δ*A*, Δ*B*, and Δ*C*, respectively (in MHz). The Θ angle (in degree) is also given.

Level of theory	***A***	**Δ*A***	***B***	**Δ*B***	***C***	**Δ*C***	***Θ***
B3LYP-D3/6-31G(d,p)	2765.6	161.1	866.6	–18.8	764.7	–30.3	21.3
B3LYP-D3/6-31+G(d,p)	2519.9	–84.6	881.8	–3.6	793.5	–1.5	43.0
B3LYP-D3/6-31++G(d,p)	2532.2	–72.3	879.7	–5.7	792.1	–2.9	41.8
B3LYP-D3/6-311G(d,p)	2766.8	162.3	866.3	–19.1	765.5	–29.5	21.6
B3LYP-D3/6-311+G(d,p)	2602.0	–2.5	873.3	–12.1	786.5	–8.5	35.7
B3LYP-D3/6-311++G(d,p)	2604.6	0.1	873.1	–12.3	786.2	–8.8	35.6
B3LYP-D3/6-311G(2d,2p)	2739.0	134.5	869.7	–15.7	773.0	–22.0	24.9
B3LYP-D3/6-311+G(2d,2p)	2622.6	18.1	874.8	–10.6	787.1	–7.9	35.0
B3LYP-D3/6-311++G(2d,2p)	2624.8	20.3	874.6	–10.8	786.8	–8.2	34.8
B3LYP-D3/6-311G(df,pd)	2775.3	170.8	868.3	–17.1	767.5	–27.5	21.5
B3LYP-D3/6-311+G(df,pd)	2593.6	–10.9	877.3	–8.1	790.7	–4.3	37.3
B3LYP-D3/6-311++G(df,pd)	2595.3	–9.2	877.2	–8.2	790.5	–4.5	37.2
B3LYP-D3/6-311G(2df,2pd)	2750.3	145.8	870.1	–15.3	772.8	–22.2	24.1
B3LYP-D3/6-311+G(2df,2pd)	2626.7	22.2	875.3	–10.1	787.9	–7.1	34.7
B3LYP-D3/6-311++G(2df,2pd)	2626.9	22.4	875.3	–10.1	787.8	–7.2	34.8
B3LYP-D3/6-311G(3df,3pd)	2720.1	115.6	871.4	–14.0	777.0	–18.0	26.6
B3LYP-D3/6-311+G(3df,3pd)	2597.2	–7.3	879.0	–6.4	791.9	–3.1	37.6
B3LYP-D3/6-311++G(3df,3pd)	2598.7	–5.8	878.8	–6.6	791.7	–3.3	37.5
B3LYP-D3/aug-cc-pVDZ	2615.4	10.9	871.4	–14.0	783.9	–11.1	34.4
B3LYP-D3/cc-pVTZ	2680.5	76.0	871.3	–14.1	781.1	–13.9	30.1
B3LYP-D3/aug-cc-pVTZ	2605.0	0.5	877.0	–8.4	790.2	–4.8	36.8
B3LYP-D3BJ/6-31G(d,p)	2712.2	107.7	869.2	–16.2	773.9	–21.1	26.2
B3LYP-D3BJ/6-31+G(d,p)	2460.4	–144.1	898.1	12.7	802.0	7.0	50.2
B3LYP-D3BJ/6-31++G(d,p)	2464.8	–139.7	896.9	11.5	801.6	6.6	49.7
B3LYP-D3BJ/6-311G(d,p)	2460.8	–143.7	906.6	21.2	807.4	12.4	51.5
B3LYP-D3BJ/6-311+G(d,p)	2518.2	–86.3	887.9	2.5	798.4	3.4	44.4
B3LYP-D3BJ/6-311++G(d,p)	2530.3	–74.2	885.6	0.2	797.0	2.0	43.2
B3LYP-D3BJ/6-311G(2d,2p)	2690.8	86.3	873.0	–12.4	781.4	–13.6	29.5
B3LYP-D3BJ/6-311+G(2d,2p)	2567.3	–37.2	883.6	–1.8	795.7	0.7	40.6
B3LYP-D3BJ/6-311++G(2d,2p)	2571.5	–33.0	882.9	–2.5	795.2	0.2	40.3
B3LYP-D3BJ/6-311G(df,pd)	2367.9	–236.6	961.6	76.2	819.3	24.3	69.7
B3LYP-D3BJ/6-311+G(df,pd)	2497.9	–106.6	896.6	11.2	803.6	8.6	47.6
B3LYP-D3BJ/6-311++G(df,pd)	2508.5	–96.0	894.1	8.7	802.5	7.5	46.5

B3LYP-D3BJ/6-311G(2df,2pd)	2703.2	98.7	873.1	–12.3	781.0	–14.0	28.6
B3LYP-D3BJ/6-311+G(2df,2pd)	2570.7	–33.8	884.0	–1.4	796.5	1.5	40.4
B3LYP-D3BJ/6-311++G(2df,2pd)	2572.5	–32.0	883.7	–1.7	796.3	1.3	40.3
B3LYP-D3BJ/6-311G(3df,3pd)	2677.3	72.8	874.7	–10.7	784.5	–10.5	30.7
B3LYP-D3BJ/6-311+G(3df,3pd)	2523.3	–81.2	893.5	8.1	802.4	7.4	45.4
B3LYP-D3BJ/6-311++G(3df,3pd)	2525.3	–79.2	893.0	7.6	802.2	7.2	45.2
B3LYP-D3BJ/cc-pVDZ	2775.3	170.8	865.3	–20.1	764.1	–30.9	20.7
B3LYP-D3BJ/aug-cc-pVDZ	2560.6	–43.9	879.7	–5.7	792.6	–2.4	40.0
B3LYP-D3BJ/cc-pVTZ	2618.2	13.7	877.9	–7.5	791.0	–4.0	36.0
B3LYP-D3BJ/aug-cc-pVTZ	2542.1	–62.4	888.3	2.9	799.5	4.5	43.3
CAM-B3LYP-D3BJ/6-311G(d,p)	2802.0	197.5	874.1	–11.3	771.4	–23.6	20.8
CAM-B3LYP-D3BJ/6-311+G(d,p)	2643.4	38.9	880.2	–5.2	791.9	–3.1	34.3
CAM-B3LYP-D3BJ/aug-cc-pVDZ	2706.6	102.1	879.5	–5.9	788.5	–6.5	30.1
CAM-B3LYP-D3BJ/aug-cc-pVTZ	2644.8	40.3	879.4	–6.0	790.6	–4.4	34.1
CAM-B3LYP-D3BJ-cc-pVDZ	2644.5	40.0	880.2	–5.2	791.8	–3.2	34.3
CAM-B3LYP-D3BJ/cc-pVTZ	2848.9	244.4	872.5	–12.9	762.7	–32.3	16.1
M06-2X/6-31G(d,p)	2840.6	236.1	877.0	–8.4	767.0	–28.0	17.1
M06-2X/6-31+G(d,p)	2710.2	105.7	878.2	–7.2	783.1	–11.9	28.0
M06-2X/6-31++G(d,p)	2712.9	108.4	878.0	–7.4	782.7	–12.3	27.8
M06-2X/6-311G(d,p)	2832.2	227.7	876.7	–8.7	769.5	–25.5	18.3
M06-2X/6-311+G(d,p)	2726.6	122.1	879.1	–6.3	783.8	–11.2	27.3
M06-2X/6-311++G(d,p)	2726.1	121.6	879.1	–6.3	783.8	–11.2	27.4
M06-2X/6-311G(df,pd)	2839.1	234.6	878.1	–7.3	771.0	–24.0	18.3
M06-2X/6-311+G(df,pd)	2730.0	125.5	880.7	–4.7	785.7	–9.3	27.6
M06-2X/6-311++G(df,pd)	2728.4	123.9	880.9	–4.5	785.9	–9.1	27.7
M06-2X/6-311G(3df,3pd)	2787.6	183.1	880.8	–4.6	780.1	–14.9	23.2
M06-2X/6-311+G(3df,3pd)	2729.8	125.3	881.9	–3.5	787.3	–7.7	28.3
M06-2X/6-311++G(3df,3pd)	2729.9	125.4	881.9	–3.5	787.3	–7.7	28.3
M06-2X/cc-pVDZ	2869.3	264.8	876.0	–9.4	762.7	–32.3	14.5
M06-2X/aug-cc-pVDZ	2718.3	113.8	879.2	–6.2	784.2	–10.8	28.1
M06-2X/cc-pVTZ	2753.1	148.6	880.6	–4.8	784.2	–10.8	26.2
M06-2X/aug-cc-pVTZ	2714.5	110.0	882.1	–3.3	789.1	–5.9	29.7
MP2/6-31G(d,p)	2383.1	–221.4	971.7	86.3	827.2	32.2	70.9
MP2/6-31+G(d,p)	2412.1	–192.4	937.2	51.8	819.0	24.0	61.5
MP2/6-31++G(d,p)	2418.0	–186.5	934.8	49.4	818.7	23.7	60.6
MP2/6-311G(d,p)	2388.7	–215.8	968.7	83.3	827.4	32.4	69.4
MP2/6-311+G(d,p)	2465.6	–138.9	918.3	32.9	815.0	20.0	53.0
MP2/6-311++G(d,p)	2480.4	–124.1	913.5	28.1	813.2	18.2	51.0
MP2/6-311G(2d,2p)	2726.9	122.4	881.6	–3.8	786.9	–8.1	27.6
MP2/6-311+G(2d,2p)	2611.6	7.1	889.9	4.5	800.4	5.4	37.9
MP2/6-311++G(2d,2p)	2612.9	8.4	889.7	4.3	800.3	5.3	37.8
MP2/6-311G(df,pd)	2412.1	–192.4	973.1	87.7	833.4	38.4	68.5
MP2/6-311+G(df,pd)	2471.3	–133.2	930.1	44.7	822.1	27.1	55.1
MP2/6-311++G(df,pd)	2481.1	–123.4	926.5	41.1	820.9	25.9	53.8
MP2/6-311G(2df,2pd)	2747.7	143.2	885.7	0.3	789.5	–5.5	26.7
MP2/6-311+G(2df,2pd)	2615.3	10.8	895.2	9.8	805.3	10.3	38.5
MP2/6-311++G(2df,2pd)	2614.7	10.2	895.3	9.9	805.4	10.4	38.6
MP2/6-311G(3df,3pd)	2709.9	105.4	887.2	1.8	793.7	–1.3	29.6

MP2/6-311+G(3df,3pd)	2473.1	–131.4	931.8	46.4	823.1	28.1	55.5
MP2/6-311++G(3df,3pd)	2472.4	–132.1	932.0	46.6	823.2	28.2	55.5
MP2/cc-pVDZ	2746.1	141.6	871.4	–14.0	772.4	–22.6	23.1
MP2/aug-cc-pVDZ	2387.5	–217.0	948.7	63.3	820.2	25.2	65.7
MP2/cc-pVTZ	2628.7	24.2	891.7	6.3	802.3	7.3	37.1
MP2/aug-cc-pVTZ	2501.1	–103.4	917.9	32.5	817.6	22.6	50.8
ωB97X-D/6-311G(d,p)	2599.5	–5.0	883.2	–2.2	795.7	0.7	37.8
ωB97X-D/6-311+G(d,p)	2602.2	–2.3	882.9	–2.5	795.3	0.3	37.6
ωB97X-D/6-311++G(d,p)	2473.4	–131.1	913.2	27.8	812.6	17.6	51.6
ωB97XD/aug-cc-pVDZ	2606.4	1.9	880.7	–4.7	792.9	–2.1	36.8
ωB97XD/aug-cc-pVTZ	2600.1	–4.4	886.7	1.3	799.1	4.1	39.0
ωB97XD/cc-pVDZ	2781.9	177.4	870.0	–15.4	769.0	–26.0	21.3
ωB97XD/cc-pVTZ	2657.1	52.6	880.5	–4.9	792.3	–2.7	33.7
Expt.	**2604.5**		**885.4**		**795.0**		

Table S-9. The rotational constants *A*, *B*, *C* (in MHz) of the C_1 conformer of ethyl 2-methylpentanoate calculated at different levels of theory and their deviations to the experimental values (calc.–exp.) Δ*A*, Δ*B*, and Δ*C*, respectively (in MHz). The Θ angle (in degree) is also given.

Level of theory	***A***	**Δ*A***	***B***	**Δ*B***	***C***	**Δ*C***	***Θ***
B3LYP-D3/6-31G(d,p)	1473.4	–533.8	819.4	165.3	604.8	38.4	77.4
B3LYP-D3/6-31+G(d,p)	1830.8	–176.4	673.4	19.3	571.0	4.6	47.3
B3LYP-D3/6-31++G(d,p)	1829.1	–178.1	673.9	19.8	571.1	4.7	47.4
B3LYP-D3/6-311G(d,p)	1513.2	–494.0	795.8	141.7	601.2	34.8	73.5
B3LYP-D3/6-311+G(d,p)	2040.8	33.6	638.8	–15.3	558.3	–8.1	35.1
B3LYP-D3/6-311++G(d,p)	2039.8	32.6	639.0	–15.1	558.3	–8.1	35.2
B3LYP-D3/6-311G(2d,2p)	1560.7	–446.5	775.7	121.6	599.0	32.6	69.2
B3LYP-D3/6-311+G(2d,2p)	2054.6	47.4	639.9	–14.2	559.2	–7.2	34.8
B3LYP-D3/6-311++G(2d,2p)	2055.9	48.7	639.8	–14.3	559.1	–7.3	34.7
B3LYP-D3/6-311G(df,pd)	1527.6	–479.6	792.6	138.5	602.2	35.8	72.4
B3LYP-D3/6-311+G(df,pd)	2013.5	6.3	645.2	–8.9	562.0	–4.4	37.0
B3LYP-D3/6-311++G(df,pd)	2009.0	1.8	646.0	–8.1	562.3	–4.1	37.3
B3LYP-D3/6-311G(2df,2pd)	1551.7	–455.5	781.5	127.4	600.6	34.2	70.3
B3LYP-D3/6-311+G(2df,2pd)	2062.4	55.2	639.7	–14.4	559.6	–6.8	34.5
B3LYP-D3/6-311++G(2df,2pd)	2061.8	54.6	639.8	–14.3	559.6	–6.8	34.5
B3LYP-D3/6-311G(3df,3pd)	2216.7	209.5	624.1	–30.0	550.3	–16.1	26.0
B3LYP-D3/6-311+G(3df,3pd)	1985.6	–21.6	651.1	–3.0	564.8	–1.6	38.8
B3LYP-D3/6-311++G(3df,3pd)	1991.3	–15.9	650.2	–3.9	564.5	–1.9	38.5
B3LYP-D3/cc-pVDZ	1445.1	–562.1	837.1	183.0	605.7	39.3	81.9
B3LYP-D3/aug-cc-pVDZ	2068.2	61.0	634.9	–19.2	556.2	–10.2	33.4
B3LYP-D3/cc-pVTZ	2160.0	152.8	628.2	–25.9	553.3	–13.1	29.3
B3LYP-D3/aug-cc-pVTZ	2019.3	12.1	645.3	–8.8	562.2	–4.2	36.9
B3LYP-D3BJ/6-31G(d,p)	1510.9	–496.3	799.8	145.7	603.3	36.9	73.3
B3LYP-D3BJ/6-31+G(d,p)	1749.5	–257.7	696.2	42.1	578.6	12.2	52.9
B3LYP-D3BJ/6-31++G(d,p)	1744.7	–262.5	697.6	43.5	579.0	12.6	53.3

B3LYP-D3BJ/6-311G(d,p)	1548.8	–458.4	779.6	125.5	599.6	33.2	70.0
B3LYP-D3BJ/6-311+G(d,p)	1857.0	–150.2	672.5	18.4	572.3	5.9	46.0
B3LYP-D3BJ/6-311++G(d,p)	1866.6	–140.6	670.5	16.4	571.6	5.2	45.5
B3LYP-D3BJ/6-311G(2d,2p)	1614.1	–393.1	754.4	100.3	596.0	29.6	64.4
B3LYP-D3BJ/6-311+G(2d,2p)	1926.5	–80.7	662.1	8.0	569.3	2.9	42.2
B3LYP-D3BJ/6-311++G(2d,2p)	1930.8	–76.4	661.3	7.2	568.9	2.5	42.0
B3LYP-D3BJ/6-311G(df,pd)	1561.4	–445.8	777.9	123.8	600.7	34.3	69.2
B3LYP-D3BJ/6-311+G(df,pd)	1825.4	–181.8	682.9	28.8	576.6	10.2	48.4
B3LYP-D3BJ/6-311++G(df,pd)	1833.7	–173.5	681.0	26.9	576.0	9.6	47.9
B3LYP-D3BJ/6-311G(2df,2pd)	1604.4	–402.8	759.6	105.5	597.7	31.3	65.4
B3LYP-D3BJ/6-311+G(2df,2pd)	1932.9	–74.3	661.7	7.6	569.7	3.3	41.9
B3LYP-D3BJ/6-311++G(2df,2pd)	1936.5	–70.7	661.1	7.0	569.4	3.0	41.8
B3LYP-D3BJ/6-311G(3df,3pd)	2141.5	134.3	632.8	–21.3	556.4	–10.0	30.3
B3LYP-D3BJ/6-311+G(3df,3pd)	1841.4	–165.8	681.1	27.0	576.5	10.1	47.6
B3LYP-D3BJ/6-311++G(3df,3pd)	1845.0	–162.2	680.3	26.2	576.3	9.9	47.4
B3LYP-D3BJ/cc-pVDZ	1474.8	–532.4	820.1	166.0	605.0	38.6	78.2
B3LYP-D3BJ/aug-cc-pVDZ	1925.0	–82.2	658.7	4.6	567.3	0.9	41.6
B3LYP-D3BJ/cc-pVTZ	2036.3	29.1	644.8	–9.3	562.7	–3.7	36.1
B3LYP-D3BJ/aug-cc-pVTZ	1883.9	–123.3	670.9	16.8	572.9	6.5	44.9
CAM-B3LYP-D3BJ/6-311G(d,p)	1545.9	–461.3	794.7	140.6	605.7	39.3	71.9
CAM-B3LYP-D3BJ/6-311+G(d,p)	2082.6	75.4	642.1	–12.0	562.1	–4.3	33.8
CAM-B3LYP-D3BJ/aug-cc-pVDZ	2173.4	166.2	635.1	–19.0	559.1	–7.3	29.6
CAM-B3LYP-D3BJ/aug-cc-pVTZ	2072.6	65.4	643.2	–10.9	562.4	–4.0	34.2
CAM-B3LYP-D3BJ-cc-pVDZ	2079.4	72.2	642.6	–11.5	562.4	–4.0	34.0
CAM-B3LYP-D3BJ/cc-pVTZ	1475.9	–531.3	834.0	179.9	609.9	43.5	80.1
M06-2X/6-31G(d,p)	1484.6	–522.6	840.6	186.5	616.7	50.3	77.8
M06-2X/6-31+G(d,p)	1555.5	–451.7	792.0	137.9	607.0	40.6	70.0
M06-2X/6-31++G(d,p)	1554.9	–452.3	792.4	138.3	607.1	40.7	70.1
M06-2X/6-311G(d,p)	1502.7	–504.5	829.8	175.7	615.3	48.9	76.0
M06-2X/6-311+G(d,p)	1546.4	–460.8	800.7	146.6	609.6	43.2	71.0
M06-2X/6-311++G(d,p)	1548.0	–459.2	799.9	145.8	609.5	43.1	70.9
M06-2X/6-311G(df,pd)	1510.2	–497.0	829.1	175.0	616.3	49.9	75.4
M06-2X/6-311+G(df,pd)	1559.2	–448.0	797.2	143.1	609.9	43.5	70.1
M06-2X/6-311++G(df,pd)	1559.9	–447.3	796.8	142.7	609.8	43.4	70.0
M06-2X/6-311G(3df,3pd)	1548.0	–459.2	808.5	154.4	613.1	46.7	71.9
M06-2X/6-311+G(3df,3pd)	1579.3	–427.9	789.2	135.1	608.7	42.3	68.5
M06-2X/6-311++G(3df,3pd)	1580.5	–426.7	788.6	134.5	608.5	42.1	68.4
M06-2X/cc-pVDZ	1468.7	–538.5	850.7	196.6	616.8	50.4	80.7
M06-2X/aug-cc-pVDZ	1535.3	–471.9	808.4	154.3	612.1	45.7	71.8
M06-2X/cc-pVTZ	1561.5	–445.7	798.8	144.7	610.8	44.4	70.3
M06-2X/aug-cc-pVTZ	1606.8	–400.4	775.0	120.9	605.6	39.2	66.0
MP2/6-31G(d,p)	1534.5	–472.7	802.8	148.7	609.6	43.2	72.0
MP2/6-31+G(d,p)	1602.3	–404.9	762.7	108.6	599.9	33.5	65.4
MP2/6-31++G(d,p)	1611.5	–395.7	758.7	104.6	599.1	32.7	64.5
MP2/6-311G(d,p)	1551.4	–455.8	794.6	140.5	608.0	41.6	70.1
MP2/6-311+G(d,p)	1660.6	–346.6	741.4	87.3	595.5	29.1	60.1
MP2/6-311++G(d,p)	1680.9	–326.3	734.0	79.9	593.6	27.2	58.4
MP2/6-311G(2d,2p)	1559.1	–448.1	798.1	144.0	610.7	44.3	70.0

MP2/6-311+G(2d,2p)	1958.3	–48.9	666.9	12.8	573.8	7.4	40.4
MP2/6-311++G(2d,2p)	1958.9	–48.3	666.7	12.6	573.7	7.3	40.4
MP2/6-311G(df,pd)	1572.2	–435.0	795.8	141.7	611.7	45.3	69.1
MP2/6-311+G(df,pd)	1690.7	–316.5	740.0	85.9	597.9	31.5	58.6
MP2/6-311++G(df,pd)	1704.4	–302.8	735.3	81.2	596.7	30.3	57.5
MP2/6-311G(2df,2pd)	1566.2	–441.0	801.0	146.9	613.2	46.8	70.1
MP2/6-311+G(2df,2pd)	1964.3	–42.9	670.3	16.2	576.6	10.2	40.7
MP2/6-311++G(2df,2pd)	1961.8	–45.4	670.6	16.5	576.8	10.4	40.8
MP2/6-311G(3df,3pd)	1604.5	–402.7	780.8	126.7	609.5	43.1	66.0
MP2/6-311+G(3df,3pd)	1693.5	–313.7	741.1	87.0	599.1	32.7	58.3
MP2/6-311++G(3df,3pd)	1693.3	–313.9	741.2	87.1	599.1	32.7	58.3
MP2/cc-pVDZ	1488.9	–518.3	819.8	165.7	608.8	42.4	76.4
MP2/aug-cc-pVDZ	1560.2	–447.0	779.6	125.5	603.6	37.2	67.2
MP2/cc-pVTZ	1650.2	–357.0	756.2	102.1	602.1	35.7	62.1
MP2/aug-cc-pVTZ	1689.6	–317.6	740.5	86.4	598.5	32.1	58.5
ωB97X-D/6-311G(d,p)	1645.4	–361.8	743.7	89.6	594.7	28.3	61.8
ωB97X-D/6-311+G(d,p)	1647.3	–359.9	742.9	88.8	594.5	28.1	61.7
ωB97X-D/6-311++G(d,p)	1532.0	–475.2	799.6	145.5	606.3	39.9	72.5
ωB97XD/aug-cc-pVDZ	1671.0	–336.2	732.8	78.7	592.0	25.6	59.3
ωB97XD/aug-cc-pVTZ	1993.7	–13.5	656.4	2.3	569.2	2.8	39.3
ωB97XD/cc-pVDZ	1480.7	–526.5	826.4	172.3	608.8	42.4	78.2
ωB97XD/cc-pVTZ	1648.8	–358.4	747.8	93.7	597.2	30.8	62.1
Expt.	**2007.2**		**654.1**		**566.4**		