

## Supplementary Information

### Structural and Thermochemical Studies of Pyrrolidine borane and Piperidine borane by Gas Electron Diffraction and Quantum Chemical Calculations

Aliyu M. Ja'o,<sup>1</sup> Derek A. Wann,<sup>2</sup> Conor D. Rankine,<sup>2</sup> João P. F. Nunes,<sup>2</sup> Jean-Claude Guillemin<sup>3</sup> and Sarah L. Masters<sup>1\*</sup>

<sup>1</sup> School of Physical and Chemical Sciences, University of Canterbury, Private Bag 4100, Christchurch 8140, New Zealand

<sup>2</sup> Department of Chemistry, University of York, Heslington, York, YO10 5DD, United Kingdom

<sup>3</sup> Univ Rennes, École Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR6226, F-35000 Rennes, France

\*Correspondence: [sarah.masters@canterbury.ac.nz](mailto:sarah.masters@canterbury.ac.nz)

## Supplementary Information Part I:

### Data for study of PYB and PIB using models based on M06-2X optimized geometries

#### Data Collection

The sample and nozzle in-line heating elements in the University of York gas electron diffractometer (described in detail by Rankine, Nunes, and Wann *et al.*; *J. Phys. Chem. A*, 2018, 122, 5656-5665) are controlled by proportional-integral-derivative (PID) drivers that are able to provide temperature stability of  $\pm 1$  K. As the set temperatures were the same at the long and short nozzle-to-image-plate distances, and data were acquired after allowing the sample and nozzle to equilibrate at the temperature for ca. 15 minutes after the set temperature was reached, there would have been no more than ca. 2 K difference between the sample temperature at the long and short nozzle-to-image-plate distances. The sample was replaced between data acquisition at the long and short nozzle-to-image-plate distances with aliquots from the same batch. Therefore, the vapour composition should be comparable in both experiments – at least with respect to the sensitivity of the GED technique. An increase in pressure on exposure of the sample to the vacuum was observed. The baseline pressure of the GED experiments was ca.  $1 \times 10^{-6}$  Torr; with the sample admission valve open ca. 5%, a pressure of ca.  $1 \times 10^{-5}$  Torr was recorded in the

diffraction chamber. This is commensurate with many other GED experiments and not unexpected.

Table S1: Experimental parameters for the GED data collection, reduction and refinement of **PYB** and **PIB**.

Dataset	<b>PYB</b>		<b>PIB</b>	
	Short	Long	Short	Long
Nozzle-to-plate distance / mm	234.5	487.0	234.5	487.0
$T_{\text{nozzle, av}} / \text{K}$	406	397	410	407
$T_{\text{sample, av}} / \text{K}$	398	388	404	397
Electron wavelength / pm	5.85	5.85	5.85	5.85
Exposure Time / s	240.0	120.0	240.0	120.0
$\Delta s / \text{nm}^{-1}$	2.0	1.0	2.0	1.0
$s_{\text{min}} / \text{nm}^{-1}$	100.0	38.0	100.0	38.0
$sw_1 / \text{nm}^{-1}$	120.0	58.0	120.0	58.0
$sw_2 / \text{nm}^{-1}$	204.0	129.0	204.0	154.0
$s_{\text{max}} / \text{nm}^{-1}$	238.0	150.0	238.0	179.0
Correlation parameter	0.4745	0.4990	0.4715	0.4991
Scale factor ( $k$ ) <sup>A</sup>	0.0272(7)	0.0131(2)	0.0179(3)	0.0073(1)

<sup>a</sup> Values in parentheses are the estimated standard deviations.

Table S2: Least-squares correlation matrix<sup>a</sup> ( $\times 100$ ) for the refinement of **PYB**.

	$P_{15}$	$u_{10}$	$u_{15}$	$u_{66}$	$k_1$
$p_3$			57		
$p_6$		54			
$p_8$	67				
$u_2$					69
$u_{61}$				54	

<sup>a</sup> Only values  $\geq 50\%$  are included in the least-squares correlation matrix.  $k_1$  and  $k_2$  are the scale factors.

Table S3: Least-squares correlation matrix<sup>a</sup> ( $\times 100$ ) for the refinement of **PIB**.

	$p_{12}$	$p_{20}$	$u_5$	$u_{10}$	$u_{28}$	$u_{40}$	$k_1$
$p_7$			63				
$p_{11}$	-64	53					
$p_{12}$		-88					
$u_4$							61
$u_9$				-57			
$u_{21}$					-66		
$u_{37}$						-64	

<sup>a</sup> Only values  $\geq 50\%$  are included in the least-squares correlation matrix.  $k_1$  is a scale factor

Table S4: Calculated coordinates at the M06-2X/aug-cc-pVDZ level for **PYB**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-1.50339	-0.77611	-0.02122
C	-1.50341	0.77610	-0.02110
C	-0.02884	-1.16653	0.15202
H	-1.89758	-1.16288	-0.96757
H	-2.11742	-1.19183	0.78346
C	-0.02882	1.16655	0.15192
H	-2.11727	1.19167	0.78378
H	-1.89782	1.16301	-0.96730
N	0.74595	-0.00002	-0.33688
H	0.27988	-2.06314	-0.39175
H	0.24508	-1.28550	1.20636
H	0.24519	1.28569	1.20622
H	0.27983	2.06309	-0.39200
B	2.31267	-0.00000	0.07833
H	2.31125	0.00003	1.29859
H	2.78045	1.01719	-0.40271
H	2.78045	-1.01722	-0.40266
H	0.70967	-0.00006	-1.35756

Table S5: Calculated coordinates at the M06-2X/cc-pVTZ level for **PYB**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-1.50109	-0.77479	-0.02161
C	-1.50111	0.77478	-0.02150
C	-0.02962	-1.16344	0.15352
H	-1.89126	-1.15756	-0.96341
H	-2.11460	-1.18989	0.77427
C	-0.02961	1.16346	0.15343
H	-2.11447	1.18973	0.77458
H	-1.89149	1.15769	-0.96315
N	0.74423	-0.00001	-0.33756
H	0.27678	-2.05817	-0.38111
H	0.24067	-1.28006	1.20228
H	0.24078	1.28023	1.20215
H	0.27673	2.05812	-0.38135
B	2.31283	-0.00000	0.07665
H	2.31270	0.00002	1.28722
H	2.77772	1.00877	-0.39996
H	2.77773	-1.00879	-0.39992
H	0.70349	-0.00006	-1.35491

Table S6: Calculated coordinates at the M06-2X/aug-cc-pVTZ level for **PYB**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-1.50092	-0.77474	-0.02149
C	-1.50093	0.77473	-0.02145
C	-0.02955	-1.16352	0.15332
H	-1.89097	-1.15742	-0.96331
H	-2.11431	-1.18971	0.77454
C	-0.02954	1.16352	0.15329
H	-2.11427	1.18966	0.77463
H	-1.89105	1.15746	-0.96323
N	0.74419	-0.00000	-0.33749
H	0.27680	-2.05774	-0.38213
H	0.24082	-1.28039	1.20200
H	0.24085	1.28044	1.20196
H	0.27678	2.05773	-0.38220
B	2.31200	0.00000	0.07693
H	2.31201	0.00001	1.28764
H	2.77726	1.00889	-0.39976
H	2.77726	-1.00889	-0.39974
H	0.70514	-0.00002	-1.35465

Table S7: Calculated coordinates at the CBS–QB3 level for **TS1** (of **PYB**).

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-0.20930	-1.18062	-0.20607
C	-0.20846	1.22158	0.04747
H	-0.16318	-1.41972	-1.27992
H	0.14659	-2.06029	0.33785
H	-0.13678	1.77884	0.98913
H	0.14364	1.88714	-0.74838
N	0.60930	-0.00537	0.10955
H	1.63344	-0.13321	1.07313
B	2.13966	0.01831	-0.20452
H	2.61238	-0.15289	1.09258
H	2.57251	1.09499	-0.48883
H	2.55548	-0.95493	-0.75943
C	-1.64953	0.73003	-0.21252
H	-2.39461	1.31223	0.33298
C	-1.62192	-0.75235	0.19859
H	-2.40123	-1.34460	-0.28546
H	-1.74445	-0.85144	1.28170
H	-1.88353	0.81232	-1.27784

Table S8: Calculated coordinates at the CBS–QB3 level for **PYB...BH<sub>3</sub>**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-0.51386	-0.94776	0.61134
C	-1.07376	1.22904	-0.14402
C	-2.34198	0.36314	-0.32438
C	-1.88590	-1.09558	-0.04991
H	0.16038	-1.79049	0.47354
H	-0.59285	-0.72842	1.67759
H	-1.09682	1.79785	0.78594
H	-0.87838	1.92246	-0.96038
H	-3.11572	0.67862	0.37707
H	-2.75690	0.46457	-1.32824
H	-2.58433	-1.64255	0.58446
H	-1.79347	-1.65230	-0.98612
N	0.07452	0.26837	-0.03610
H	0.36859	0.00012	-0.97861
B	1.37937	0.89151	0.64021
H	1.21164	0.94057	1.83017
H	2.32843	0.04127	0.57288
H	1.66061	1.92056	0.10497
B	2.78440	-0.56486	-0.56619
H	3.94841	-0.32252	-0.42857
H	2.43923	-1.69025	-0.30749
H	2.27840	-0.08334	-1.54814



Table S9: Calculated coordinates at the CBS–QB3 level for **TS2** (of **PYB**).

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-0.65754	-0.92815	0.80910
C	-0.86921	1.18234	-0.39021
C	-2.23873	0.49414	-0.29238
C	-1.88264	-0.98902	-0.10485
H	-0.00202	-1.79647	0.72439
H	-0.95397	-0.82774	1.85756
H	-0.86508	2.18906	0.02716
H	-0.53539	1.25325	-1.43251
H	-2.78196	0.86066	0.58383
H	-2.85907	0.68143	-1.17037
H	-2.69543	-1.57555	0.32655
H	-1.61661	-1.44093	-1.06564
N	0.07051	0.29809	0.36711
H	0.99520	-0.15381	-0.63803
B	1.16749	0.84757	1.16633
H	1.56571	0.21048	2.08510
H	2.61907	0.44575	0.07434
H	1.42405	2.00138	1.03833
B	2.62745	-0.49300	-0.72589
H	3.40145	-0.33921	-1.62793
H	2.59878	-1.57113	-0.20598
H	1.48792	-0.34916	-1.40603

Table S10: Calculated coordinates at the M06-2X/aug-cc-pVDZ level for **PIB**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	1.88590	0.00000	0.27740
C	1.16073	1.25277	-0.21380
C	1.16073	-1.25277	-0.21380
H	1.90375	0.00000	1.37752
H	2.92790	0.00000	-0.06406
C	-0.30996	1.22344	0.18451
H	1.24169	1.32246	-1.30984
H	1.62059	2.15926	0.19831
C	-0.30996	-1.22344	0.18451
H	1.62059	-2.15926	0.19831
H	1.24169	-1.32246	-1.30984
N	-0.99649	0.00000	-0.29828
H	-0.86526	2.07967	-0.21064
H	-0.42743	1.22145	1.27573
H	-0.42743	-1.22145	1.27573
H	-0.86526	-2.07967	-0.21064
B	-2.57825	0.00000	0.08040
H	-3.03134	1.01715	-0.41407
H	-2.61567	0.00000	1.29961
H	-3.03134	-1.01715	-0.41407
H	-0.95042	0.00000	-1.31900

Table S11: Calculated coordinates at the M06-2X/cc-pVTZ level for **PIB**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-1.88185	0.00000	0.28200
C	-1.16035	-1.25042	-0.21238
C	-1.16035	1.25042	-0.21238
H	-1.89343	0.00000	1.37566
H	-2.92009	0.00000	-0.04912
C	0.30903	-1.22188	0.17968
H	-1.24396	-1.31622	-1.30187
H	-1.61815	-2.15258	0.19373
C	0.30903	1.22188	0.17968
H	-1.61815	2.15258	0.19373
H	-1.24396	1.31622	-1.30187
N	0.99503	0.00000	-0.30188
H	0.85889	-2.07405	-0.21362
H	0.42903	-1.22355	1.26432
H	0.42903	1.22355	1.26432
H	0.85889	2.07405	-0.21362
B	2.57706	0.00000	0.08569
H	3.03058	-1.00907	-0.40111
H	2.60656	0.00000	1.29526
H	3.03058	1.00907	-0.40111
H	0.95059	0.00000	-1.31957

Table S12: Calculated coordinates at the M06-2X/aug-cc-pVTZ level for **PIB**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-1.88203	0.00000	0.28146
C	-1.16014	-1.25022	-0.21227
C	-1.16014	1.25022	-0.21227
H	-1.89457	0.00000	1.37504
H	-2.91990	0.00000	-0.05069
C	0.30906	-1.22174	0.17983
H	-1.24317	-1.31555	-1.30180
H	-1.61794	-2.15260	0.19330
C	0.30906	1.22174	0.17983
H	-1.61794	2.15260	0.19330
H	-1.24317	1.31555	-1.30180
N	0.99512	0.00000	-0.30173
H	0.85885	-2.07396	-0.21341
H	0.42880	-1.22277	1.26446
H	0.42880	1.22277	1.26446
H	0.85885	2.07396	-0.21341
B	2.57642	0.00000	0.08583
H	3.03019	-1.00918	-0.40112
H	2.60628	0.00000	1.29554
H	3.03019	1.00918	-0.40112
H	0.95195	0.00000	-1.31926

Table S13: Calculated coordinates at the CBS–QB3 level for **TS1** (of **PIB**).

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	0.14558	1.21978	-0.64298
C	0.14558	-1.21978	-0.64298
H	0.78836	2.08681	-0.47752
H	-0.17986	1.25035	-1.69271
H	-0.17986	-1.25035	-1.69271
H	0.78836	-2.08681	-0.47752
N	0.92948	-0.00000	-0.42367
H	2.33848	-0.00000	-0.60678
B	1.99465	-0.00000	0.73692
H	3.13741	-0.00000	-0.05726
H	2.10164	-1.02890	1.33348
H	2.10164	1.02890	1.33348
C	-1.08466	1.26775	0.27420
H	-1.67705	2.16254	0.05469
H	-0.74842	1.35268	1.31416
C	-1.08466	-1.26776	0.27420
H	-0.74842	-1.35268	1.31416
H	-1.67705	-2.16254	0.05469
C	-1.93737	-0.00000	0.10501
H	-2.76842	-0.00000	0.81686
H	-2.38542	-0.00000	-0.89773

Table S14: Calculated coordinates at the CBS–QB3 level for **PIB...BH<sub>3</sub>**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	2.01630	-0.96050	-0.54523
C	2.52697	0.36906	0.02354
C	1.43235	1.44047	-0.05224
C	0.14218	0.96843	0.61537
C	0.71263	-1.39493	0.12444
H	1.75725	2.36553	0.43199
H	2.82557	0.22676	1.06918
H	3.41938	0.69499	-0.51706
H	1.85466	-0.86428	-1.62605
H	2.75777	-1.75331	-0.41171
H	0.28701	0.79830	1.68491
H	-0.66651	1.68804	0.49350
H	0.86294	-1.60295	1.18698
H	0.29763	-2.29306	-0.33314
H	1.22887	1.69294	-1.10008
N	-0.34234	-0.33323	0.04511
H	-0.55828	-0.16874	-0.94166
B	-1.73027	-0.82410	0.67812
H	-2.05593	-1.85946	0.18335
H	-1.63638	-0.81638	1.87698
H	-2.57929	0.11096	0.51416
B	-3.06122	0.54413	-0.69222
H	-2.91691	1.71612	-0.45025
H	-4.18096	0.12575	-0.65109
H	-2.39343	0.12945	-1.60688

Table S15: Calculated coordinates at the CBS–QB3 level for **TS2** (of **PIB**).

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	1.63324	1.05981	0.64724
C	2.39626	-0.19001	0.19298
C	1.42412	-1.35254	-0.03882
C	0.31133	-0.95752	-1.01204
C	0.51320	1.41475	-0.33449
H	1.95006	-2.22467	-0.43857
H	2.93051	0.02910	-0.74036
H	3.15401	-0.46497	0.93198
H	1.20590	0.88790	1.64196
H	2.30818	1.91616	0.73801
H	0.73950	-0.78512	-2.00941
H	-0.42764	-1.75359	-1.10525
H	0.95009	1.73253	-1.29127
H	-0.08498	2.24740	0.03948
H	0.98068	-1.66072	0.91490
N	-0.40222	0.27055	-0.57639
H	-1.06156	-0.01502	0.73966
B	-1.71230	0.55463	-1.18171
H	-2.07468	1.68738	-1.20518
H	-2.21117	-0.27165	-1.87266
H	-2.84488	0.26412	0.21201
B	-2.58659	-0.48011	1.16081
H	-2.45926	-1.62993	0.85461
H	-3.22939	-0.23737	2.14266
H	-1.40240	-0.04111	1.58984

Table S16: Energies (at CCSD(T)/CBS) and corrections for enthalpy ( $H$ ), Gibbs Free Energy ( $G$ ) and Zero Point Energy (at MP2/cc-pVTZ level; ZPE) for all the molecules involved in the calculation of the thermochemical properties of **PYB**. All the energies are in Hartrees.

Molecule	$E_{\text{CBS}}$	$H$	$G$	$ZPE$
<b>PYB</b>	-238.9160255	0.172988	0.134755	0.165366
<b>D-PYB</b>	-237.7353473	0.150209	0.112319	0.143077
Pyrrolidine	-212.3035322	0.135875	0.103851	0.130795
BH <sub>3</sub>	-26.5375896	0.030634	0.009274	0.026981
H <sub>2</sub>	-1.1744736	0.013452	-0.001327	0.010147

Table S17: Energies and corrections for enthalpy ( $H$ ), Gibbs Free Energy ( $G$ ) and Zero Point Energy (ZPE) at the CBS-QB3 level for all the molecules involved in the calculation of the thermochemical properties of **PYB**. All the energies are in Hartrees.

Molecule	$E_{\text{CBS-QB3}}$	$H$	$G$	$ZPE$
<b>PYB</b>	-238.6734468	0.170901	0.131769	0.163127
<b>D-PYB</b>	-237.5057236	0.148331	0.110513	0.141161
Pyrrolidine	-212.0992566	0.135134	0.100381	0.129144
BH <sub>3</sub>	-26.5082740	0.029974	0.008598	0.026144
H <sub>2</sub>	-1.1627599	0.013374	-0.001421	0.010069



Table S18: Energies (at CCSD(T)/CBS) and corrections for enthalpy ( $H$ ), Gibbs Free Energy ( $G$ ) and Zero Point Energy (at MP2/cc-pVTZ level; ZPE) for all the molecules involved in the calculation of the thermochemical properties of **PIB**. All the energies are in Hartrees.

Molecule	$E_{\text{CBS}}$	$H$	$G$	$ZPE$
<b>PIB</b>	-278.1831263	0.203284	0.164397	0.195065
<b>D-PIB</b>	-277.0017623	0.180576	0.142799	0.172952
Piperidine	-251.5676800	0.167021	0.131881	0.160509
BH <sub>3</sub>	-26.5375896	0.030634	0.009274	0.026981
H <sub>2</sub>	-1.1744736	0.013452	-0.001327	0.010147

Table S19: Energies and corrections for enthalpy ( $H$ ), Gibbs Free Energy ( $G$ ) and Zero Point Energy (ZPE) at the CBS-QB3 level for all the molecules involved in the calculation of the thermochemical properties of **PIB**. All the energies are in Hartrees.

Molecule	$E_{\text{CBS-QB3}}$	$H$	$G$	$ZPE$
<b>PIB</b>	-277.9007379	0.200915	0.161814	0.192600
<b>D-PIB</b>	-276.7337406	0.178396	0.140476	0.170711
Piperidine	-251.3254254	0.164907	0.129593	0.158315
BH <sub>3</sub>	-26.5082740	0.029974	0.008598	0.026144
H <sub>2</sub>	-1.1627599	0.013374	-0.001421	0.010069

Table S20: Refined ( $r_{h1}$ ) and calculated ( $r_e$ ) geometric parameters for **PYB**.

Parameter		M06-2X/aug- cc-pVTZ ( $r_e$ )	SARACEN ( $r_{h1}$ )	Restraint
$p_1$	$r_{B-H}$ av	121	121.4(9)	121.0(8)
$p_2$	$r_{B-N}$	162.2	162.8(5)	162.2(5)
$p_3$	$r_{N-C}$	148.1	147.9(3)	-
$p_4$	$r_{C-C}$ av	153.2	153.2(4)	153.2(4)
$p_5$	$r_{N-H}$	101.8	101.7(8)	101.8(7)
$p_6$	$r_{C-H}$ av	108.8	109.6(3)	-
$p_7$	$\angle N-B-H$ av	105.4	106.0(5)	-
$p_8$	$\angle C(6)-N(5)-B(1)$	114.9	114.9(2)	114.9(2)
$p_9$	$\angle C(8)-C(6)-N(5)$	105.3	105.3(2)	105.3(2)
$p_{10}$	$\angle H(10)-N(5)-B(1)$	107	107.3(5)	107(4)
$p_{11}$	av btw $\angle H(11)-C(6)-N(5)$ and $\angle H(12)-C(6)-N(5)$	107.8	107.7(2)	107.8(2)
$p_{12}$	diff btw $\angle H(11)-C(6)-N(5)$ and $\angle H(12)-C(6)-N(5)/2$	1.9	2.0(2)	1.9(2)
$p_{13}$	av btw $\angle H(15)-C(8)-C(6)$ and $\angle H(16)-C(8)-C(6)$	111	111.0(2)	111.0(2)
$p_{14}$	diff btw $\angle H(15)-C(8)-C(6)$ and $\angle H(16)-C(8)-C(6)/2$	0.3	0.2(2)	0.3(2)
$p_{15}$	$\phi C(6)-N(5)-B(1)-H(2)$	60	60.2(6)	-
$p_{16}$	$\phi C(8)-C(6)-N(5)-B(1)$	-165.3	-166.0(4)	-165.3(4)
$p_{17}$	$\phi H(11)-C(6)-N(5)-B(1)$	-46.5	-46.4(3)	-46.5(3)
$p_{18}$	$\phi H(12)-C(6)-N(5)-B(1)$	70.3	70.3(6)	70.3(5)
$p_{19}$	$\phi H(15)-C(8)-C(6)-N(5)$	145.6	145.6(6)	145.6(5)
$p_{20}$	$\phi H(16)-C(8)-C(6)-N(5)$	-95.3	-95.4(3)	-95.3(3)

Distances in pm and angles in  $^\circ$ . Digits in parentheses are the estimated standard deviation of the last digits.

Table S21: Refined ( $r_{h1}$ ) and calculated ( $r_e$ ) geometric parameters for **PIB**.

Parameter	M06-2x/aug-cc- pVTZ ( $r_e$ )	SARACEN ( $r_{h1}$ )	Restraint
$p_1$ $r_{B-H}$ av	120.9	120.8(1)	120.9(1)
$p_2$ $r_{B-N}$	162.8	163.5(3)	162.8(3)
$p_3$ $r_{N-C}$	148.2	148.3(2)	148.2(2)
$p_4$ $r_{N-H}$	101.8	101.9(5)	101.8(4)
$p_5$ $r_{C-C}$	152.1	152.7(4)	152.1(3)
$p_6$ $r_{C(10)...N(5)}$	293.6	294.3(3)	293.6(3)
$p_7$ $r_{C-H}$ av	109.1	109.8(2)	109.1(7)
$p_8$ $\angle N-B-H$ av	105.5	105.5(2)	105.5(3)
$p_9$ $\angle C(6)-N(5)-B(1)$	111.9	112.0(3)	111.9(4)
$p_{10}$ $\angle H(11)-N(5)-B(1)$	105.2	105.2(5)	105.2(2)
$p_{11}$ $\angle C(8)-C(6)-N(5)$	112.3	111.8(4)	-
$p_{12}$ $\angle C(10)...N(5)-B(1)$	154.8	154.1(6)	-
$p_{13}$ av btw $\angle H(12)-C(6)-N(5)$ and $\angle H(13)-C(6)-N(5)$	106.5	106.3(4)	106.5(3)
$p_{14}$ diff btw $\angle H(12)-C(6)-N(5)$ and $\angle H(13)-C(6)-N(5)/2$	0.6	0.6(2)	0.6(2)
$p_{15}$ av btw $\angle H(14)-C(8)-C(6)$ and $\angle H(15)-C(8)-C(6)$	109.1	109.0(2)	109.1(5)
$p_{16}$ diff between $\angle H(14)-C(8)-C(6)$ and $\angle H(15)-C(8)-C(6)/2$	0.2	0.2(2)	0.2(2)
$p_{17}$ av btw $\angle H(20)-C(10)...N(5)$ and $\angle H(21)-C(10)...N(5)$	126.5	126.5(6)	-
$p_{18}$ diff btw $\angle H(20)-C(10)...N(5)$ and $\angle H(21)-C(10)p...N(5)/2$	24.4	24.4(8)	-
$p_{19}$ $\phi_{C(6)-N(5)-B(1)-H(2)}$	62.7	62.6(3)	62.7(1)
$p_{20}$ $\phi_{C(8)-C(6)-N(5)-B(1)}$	178.3	178.1(5)	178.3(5)
$p_{21}$ $\phi_{H(12)-C(6)-N(5)-B(1)}$	-60.1	-60.1(4)	-

$p_{22}$	$\phi\text{H}(13)\text{-C}(6)\text{-N}(5)\text{-B}(1)$	54.5	54.5(3)	-
$p_{23}$	$\phi\text{H}(14)\text{-C}(8)\text{-C}(6)\text{-N}(5)$	178.3	178.3(3)	-
$p_{24}$	$\phi\text{H}(15)\text{-C}(8)\text{-C}(6)\text{-N}(5)$	-65.3	-65.3(5)	-

---

Distances in pm and angles in  $^{\circ}$ . Digits in parentheses are the estimated standard deviation of the last digits.

Table S22. Internuclear distances ( $r_a$  / pm), refined ( $u_{\text{GED}}$ ) and theoretical ( $u_{\text{h1}}$ ) amplitudes of vibration and restraints and distance corrections ( $k_{\text{h1}}$ ) for **PYB**.<sup>a</sup>

Amp.	Atomic Pair	$r_a$	$u_{\text{GED}}$	Restraint	$k_{\text{h1}}$	$u_{\text{h1}}$
$u_1$	N(9)-H(18)	101.6(8)	7.3(8)	7.2(7)	0.4	7.2
$u_2$	C(6)-H(13)	109.8(3)	5.1(4)	7.6(8)	0.4	7.6
$u_3$	C(3)-H(10)	109.8(3)	5.1 (Tied to $u_2$ )	–	0.4	7.6
$u_4$	C(2)-H(7)	109.7(3)	5.1 (Tied to $u_2$ )	–	0.4	7.6
$u_5$	C(1)-H(5)	109.7(3)	5.1 (Tied to $u_2$ )	–	0.4	7.6
$u_6$	C(6)-H(12)	109.8(3)	5.1 (Tied to $u_2$ )	–	0.4	7.6
$u_7$	C(3)-H(11)	109.8(3)	5.1 (Tied to $u_2$ )	–	0.4	7.6
$u_8$	C(1)-H(4)	109.8(3)	5.1 (Tied to $u_2$ )	–	0.4	7.7
$u_9$	C(2)-H(8)	109.8(3)	5.1 (Tied to $u_2$ )	–	0.4	7.7
$u_{10}$	B(14)-H(17)	121.2(9)	8.5(9)	8.5(9)	0.4	8.5
$u_{11}$	B(14)-H(16)	121.2(9)	8.5 (Tied to $u_{10}$ )	–	0.4	8.5
$u_{12}$	B(14)-H(15)	121.2(9)	8.6 (Tied to $u_{10}$ )	–	0.5	8.6
$u_{13}$	C(6)-N(9)	147.9(3)	4.1(4)	5.0(5)	0.1	5.0
$u_{14}$	C(3)-N(9)	147.9(3)	4.1 (Tied to $u_{13}$ )	–	0.1	5.0
$u_{15}$	C(2)-C(6)	153.2(4)	5.0(4)	–	0.2	5.2
$u_{16}$	C(1)-C(3)	153.2(4)	5.0 (Tied to $u_{15}$ )	–	0.2	5.2
$u_{17}$	C(1)-C(2)	156.0(10)	5.1 (Tied to $u_{15}$ )	–	0.2	5.3
$u_{18}$	N(9)-B(14)	162.9(5)	6.4(6)	6.2(6)	0.3	6.2
$u_{19}$	H(4)...H(5)	175.5(8)	12.4 (Fixed)	–	0.0	12.4

$u_{20}$	H(7)...H(8)	175.5(8)	12.4 (Fixed)	–	0.0	12.4
$u_{21}$	H(12)...H(13)	177.0(8)	12.3 (Fixed)	–	0.0	12.3
$u_{22}$	H(10)...H(11)	177.0(8)	12.3 (Fixed)	–	0.0	12.3
$u_{23}$	H(16)...H(17)	201.2(16)	13.7 (Fixed)	–	0.1	13.7
$u_{24}$	H(15)...H(17)	201.2(16)	13.7 (Fixed)	–	0.1	13.7
$u_{25}$	H(15)...H(16)	201.2(16)	13.7 (Fixed)	–	0.1	13.7
$u_{26}$	C(6)...H(18)	202.5(10)	12.0(8)	–	-0.2	10.4
$u_{27}$	C(3)...H(18)	202.5(10)	12.0 (Tied to $u_{26}$ )	–	-0.2	10.4
$u_{28}$	N(9)...H(12)	205.6(5)	12.0 (Tied to $u_{26}$ )	–	-0.2	10.5
$u_{29}$	N(9)...H(11)	205.6(5)	12.0 (Tied to $u_{26}$ )	–	-0.2	10.5
$u_{30}$	N(9)...H(10)	210.7(5)	12.0 (Tied to $u_{26}$ )	–	-0.2	10.5
$u_{31}$	N(9)...H(13)	210.7(5)	12.0 (Tied to $u_{26}$ )	–	-0.2	10.5
$u_{32}$	B(14)...H(18)	215.4(9)	12.0 (Fixed)	–	0.1	12.0
$u_{33}$	C(3)...H(4)	217.0(6)	10.8 (Fixed)	–	-0.2	10.8
$u_{34}$	C(6)...H(8)	217.0(6)	10.8 (Fixed)	–	-0.2	10.8
$u_{35}$	C(6)...H(7)	217.5(6)	10.9 (Fixed)	–	-0.2	10.9
$u_{36}$	C(3)...H(5)	217.5(6)	10.9 (Fixed)	–	-0.2	10.9
$u_{37}$	C(2)...H(4)	219.6(13)	10.8 (Fixed)	–	-0.1	10.8
$u_{38}$	C(1)...H(8)	219.6(13)	10.8 (Fixed)	–	-0.1	10.8
$u_{39}$	C(2)...H(12)	219.6(7)	10.8 (Fixed)	–	-0.1	10.8
$u_{40}$	C(1)...H(11)	219.6(7)	10.8 (Fixed)	–	-0.1	10.8
$u_{41}$	C(2)...H(5)	221.6(13)	10.9 (Fixed)	–	-0.2	10.9

$u_{42}$	C(1)...H(7)	221.6(13)	10.9 (Fixed)	–	-0.2	10.9
$u_{43}$	C(1)...H(10)	221.7(8)	10.7 (Fixed)	–	-0.1	10.7
$u_{44}$	C(2)...H(13)	221.7(8)	10.7 (Fixed)	–	-0.1	10.7
$u_{45}$	N(9)...H(15)	227.4(11)	12.0(11)	12.0(10)	-0.2	12.0
$u_{46}$	N(9)...H(17)	227.4(11)	12.0 (Tied to $u_{45}$ )	–	-0.2	12.0
$u_{47}$	N(9)...H(16)	227.4(11)	12.0 (Tied to $u_{45}$ )	–	-0.2	12.0
$u_{48}$	H(13)...H(18)	230.1(12) (12)	16.8 (Fixed)	–	0.0	16.8
$u_{49}$	H(10)...H(18)	230.1(12) (12)	16.8 (Fixed)	–	0.0	16.8
$u_{50}$	H(4)...H(8)	232.7(28)	17.6 (Fixed)	–	0.3	17.6
$u_{51}$	C(3)...C(6)	232.5(10)	6.0(6)	6.4(6)	-0.1	6.4
$u_{52}$	H(5)...H(7)	238.6(26)	17.9 (Fixed)	–	0.1	17.9
$u_{53}$	C(1)...N(9)	239.1(4)	6.7(6)	–	-0.1	6.1
$u_{54}$	C(2)...N(9)	239.1(4)	6.7 (Tied to $u_{53}$ )	–	-0.1	6.1
$u_{55}$	H(5)...H(11)	240.3(11)	17.7 (Fixed)	–	0.2	17.7
$u_{56}$	H(7)...H(12)	240.3(11)	17.7 (Fixed)	–	0.2	17.7
$u_{57}$	H(12)...H(15)	245.3(17)	28.2 (Fixed)	–	2.6	28.2
$u_{58}$	H(11)...H(15)	245.3(17)	28.2 (Fixed)	–	2.6	28.2
$u_{59}$	H(8)...H(13)	240.5(13)	17.6 (Fixed)	–	0.1	17.6
$u_{60}$	H(4)...H(10)	240.5(13)	17.6 (Fixed)	–	0.1	17.6
$u_{61}$	C(2)...C(3)	244.4(5)	6.1(5)	6.1(6)	0.0	6.1
$u_{62}$	C(1)...C(6)	244.4(5)	6.1 (Tied to $u_{61}$ )	–	0.0	6.1
$u_{63}$	H(16)...H(18)	249.5(13)	20.6 (Fixed)	–	0.3	20.6

$u_{64}$	H(17)...H(18)	249.5(13)	20.6 (Fixed)	–	0.3	20.6
$u_{65}$	H(11)...H(12)	254.5(34)	24.3 (Fixed)	–	0.0	24.3
$u_{66}$	C(6)...B(14)	261.6(5)	9.1(5)	8.9(9)	-0.1	8.9
$u_{67}$	C(3)...B(14)	261.6(5)	9.1 (Tied to $u_{66}$ )	–	-0.1	8.9
$u_{68}$	C(3)...H(12)	266.6(19)	15.2 (Fixed)	–	-0.4	15.2
$u_{69}$	C(6)...H(11)	266.6(19)	15.2 (Fixed)	–	-0.4	15.2
$u_{70}$	H(12)...B(14)	267.2(8)	17.0 (Fixed)	–	0.0	17.0
$u_{71}$	H(11)...B(14)	267.2(8)	17.0 (Fixed)	–	0.0	17.0
$u_{72}$	C(2)...H(18)	266.6(11)	14.9 (Fixed)	–	-0.3	14.9
$u_{73}$	C(1)...H(18)	266.6(11)	14.9 (Fixed)	–	-0.3	14.9
$u_{74}$	H(13)...H(16)	271.8(15)	26.7 (Fixed)	–	2.3	26.7
$u_{75}$	H(10)...H(17)	271.8(15)	26.7 (Fixed)	–	2.3	26.7
$u_{76}$	H(7)...H(13)	279.0(10)	15.1 (Fixed)	–	-0.5	15.1
$u_{77}$	H(5)...H(10)	279.0(10)	15.1 (Fixed)	–	-0.5	15.1
$u_{78}$	C(6)...H(15)	286.5(13)	20.0 (Fixed)	–	0.0	20.0
$u_{79}$	C(3)...H(15)	286.5(13)	20.0 (Fixed)	–	0.0	20.0
$u_{80}$	C(6)...H(16)	286.1(12)	20.3 (Fixed)	–	0.0	20.3
$u_{81}$	C(3)...H(17)	286.1(12)	20.3 (Fixed)	–	0.0	20.3
$u_{82}$	H(8)...H(18)	284.2(14)	21.9 (Fixed)	–	0.0	21.9
$u_{83}$	H(4)...H(18)	284.2(14)	21.9 (Fixed)	–	0.0	21.9
$u_{84}$	H(11)...H(18)	287.7(9)	12.3 (Fixed)	–	-1.2	12.3
$u_{85}$	H(12)...H(18)	287.7(9)	12.3 (Fixed)	–	-1.2	12.3



$u_{86}$	H(13)...B(14)	292.8(8)	15.6 (Fixed)	–	-0.2	15.6
$u_{87}$	H(10)...B(14)	292.8(8)	15.6 (Fixed)	–	-0.2	15.6
$u_{88}$	H(5)...H(8)	293.9(12)	13.9 (Fixed)	–	-0.8	13.9
$u_{89}$	H(4)...H(7)	293.9(12)	13.9 (Fixed)	–	-0.8	13.9
$u_{90}$	H(4)...N(9)	293.9(7)	13.2 (Fixed)	–	-0.4	13.2
$u_{91}$	H(8)...N(9)	293.9(7)	13.2 (Fixed)	–	-0.4	13.2
$u_{92}$	C(1)...H(12)	296.6(11)	13.2 (Fixed)	–	-0.3	13.2
$u_{93}$	C(2)...H(11)	296.6(11)	13.2 (Fixed)	–	-0.3	13.2
$u_{94}$	H(11)...H(17)	298.0(12)	29.6 (Fixed)	–	-0.8	29.6
$u_{95}$	H(12)...H(16)	298.0(12)	29.6 (Fixed)	–	-0.8	29.6
$u_{96}$	H(4)...H(11)	304.4(7)	12.9 (Fixed)	–	-1.0	12.9
$u_{97}$	H(8)...H(12)	304.4(7)	12.9 (Fixed)	–	-1.0	12.9
$u_{98}$	H(15)...H(18)	308.8(13)	13.6 (Fixed)	–	-2.0	13.6
$u_{99}$	C(3)...H(8)	318.2(7)	11.4 (Fixed)	–	-0.4	11.4
$u_{100}$	H(4)...C(6)	318.2(7)	11.4 (Fixed)	–	-0.4	11.4
$u_{101}$	C(3)...H(7)	320.8(11)	11.0 (Fixed)	–	-0.5	11.0
$u_{102}$	H(5)...C(6)	320.8(11)	11.0 (Fixed)	–	-0.5	11.0
$u_{103}$	C(6)...H(10)	327.5(7)	9.8 (Fixed)	–	-0.9	9.8
$u_{104}$	C(3)...H(13)	327.5(7)	9.8 (Fixed)	–	-0.9	9.8
$u_{105}$	H(7)...N(9)	328.4(6)	10.3 (Fixed)	–	-0.8	10.3
$u_{106}$	H(5)...N(9)	328.4(6)	10.3 (Fixed)	–	-0.8	10.3
$u_{107}$	H(10)...H(15)	333.7(16)	26.3 (Fixed)	–	-1.3	26.3

$u_{108}$	H(13)...H(15)	333.7(16)	26.3 (Fixed)	–	-1.3	26.3
$u_{109}$	C(1)...H(13)	336.5(6)	10.2 (Fixed)	–	-0.6	10.2
$u_{110}$	C(2)...H(10)	336.5(6)	10.2 (Fixed)	–	-0.6	10.2
$u_{111}$	H(7)...H(11)	344.9(19)	17.2 (Fixed)	–	-0.4	17.2
$u_{112}$	H(5)...H(12)	344.9(19)	17.2 (Fixed)	–	-0.4	17.2
$u_{113}$	C(3)...H(16)	357.7(11)	11.6 (Fixed)	–	-2.1	11.61
$u_{114}$	C(6)...H(17)	357.7(11)	11.6 (Fixed)	–	-2.1	11.6
$u_{115}$	H(11)...H(13)	368.7(18)	16.6 (Fixed)	–	-1.5	16.6
$u_{116}$	H(10)...H(12)	368.7(18)	16.6 (Fixed)	–	-1.5	16.6
$u_{117}$	H(5)...H(18)	370.3(11)	15.7 (Fixed)	–	-1.4	15.7
$u_{118}$	H(7)...H(18)	370.3(11)	15.7 (Fixed)	–	-1.4	15.7
$u_{119}$	H(11)...H(16)	374.4(12)	18.5 (Fixed)	–	-2.8	18.5
$u_{120}$	H(12)...H(17)	374.4(12)	18.5 (Fixed)	–	-2.8	18.5
$u_{121}$	C(2)...B(14)	388.8(5)	11.4(3)	8.1(4)	-0.7	8.2
$u_{122}$	C(1)...B(14)	388.8(5)	11.4 (Tied to $u_{121}$ )	–	-0.7	8.2
$u_{123}$	H(4)...H(12)	390.2(9)	15.2 (Fixed)	–	-1.2	15.2
$u_{124}$	H(8)...H(11)	390.2(9)	15.2 (Fixed)	–	-1.2	15.2
$u_{125}$	H(4)...H(13)	392.1(14)	15.3 (Fixed)	–	-0.9	15.3
$u_{126}$	H(8)...H(10)	392.1(14)	15.3 (Fixed)	–	-0.9	15.3
$u_{127}$	H(13)...H(17)	393.3(12)	18.2 (Fixed)	–	-2.7	18.2
$u_{128}$	H(10)...H(16)	393.3(12)	18.2 (Fixed)	–	-2.7	18.2
$u_{129}$	C(1)...H(15)	412.5(13)	18.9 (Fixed)	–	-0.8	18.9

$u_{130}$	C(2)...H(15)	412.5(13)	18.9 (Fixed)	–	-0.8	18.9
$u_{131}$	H(10)...H(13)	410.4(10)	13.8 (Fixed)	–	-1.9	13.8
$u_{132}$	H(7)...H(10)	419.7(11)	13.4 (Fixed)	–	-1.3	13.4
$u_{133}$	H(5)...H(13)	419.7(11)	13.4 (Fixed)	–	-1.3	13.4
$u_{134}$	C(2)...H(16)	428.9(13)	17.9 (Fixed)	–	-1.4	17.9
$u_{135}$	C(1)...H(17)	428.9(13)	17.9 (Fixed)	–	-1.4	17.9
$u_{136}$	H(4)...B(14)	447.3(7)	14.5 (Fixed)	–	-1.3	14.5
$u_{137}$	H(8)...B(14)	447.3(7)	14.5 (Fixed)	–	-1.3	14.5
$u_{138}$	H(5)...H(15)	463.5(16)	25.8 (Fixed)	–	-0.7	25.8
$u_{139}$	H(7)...H(15)	463.5(16)	25.8 (Fixed)	–	-0.7	25.8
$u_{140}$	H(5)...B(14)	463.1(7)	14.1 (Fixed)	–	-1.5	14.1
$u_{141}$	H(7)...B(14)	463.1(7)	14.1 (Fixed)	–	-1.5	14.1
$u_{142}$	C(2)...H(17)	463.4(12)	13.4 (Fixed)	–	-2.4	13.4
$u_{143}$	C(1)...H(16)	463.4(12)	13.4 (Fixed)	–	-2.4	13.4
$u_{144}$	H(4)...H(17)	468.9(15)	23.2 (Fixed)	–	-1.3	23.2
$u_{145}$	H(8)...H(16)	468.9(15)	23.2 (Fixed)	–	-1.3	23.2
$u_{146}$	H(8)...H(15)	491.2(13)	19.7 (Fixed)	–	-2.4	19.7
$u_{147}$	H(4)...H(15)	491.2(13)	19.7 (Fixed)	–	-2.4	19.7
$u_{148}$	H(7)...H(16)	501.6(13)	23.1 (Fixed)	–	-2.5	23.1
$u_{149}$	H(5)...H(17)	501.6(13)	23.1 (Fixed)	–	-2.5	23.1
$u_{150}$	H(8)...H(17)	515.5(14)	19.4 (Fixed)	–	-2.8	19.4
$u_{151}$	H(4)...H(16)	515.5(14)	19.4 (Fixed)	–	-2.8	19.4

$u_{152}$	H(7)...H(17)	546.8(12)	16.6 (Fixed)	–	-3.7	16.6
$u_{153}$	H(5)...H(16)	546.8(12)	16.7 (Fixed)	–	-3.7	16.7

---

<sup>a</sup> All values are tabulated in pm.

Table S23. Internuclear distances ( $r_a$  / pm), refined ( $u_{\text{GED}}$ ) and theoretical ( $u_{\text{h1}}$ ) amplitudes of vibration and restraints and distance corrections ( $k_{\text{h1}}$ ) for **PIB**.<sup>a</sup>

Amp.	Atomic Pair	$r_a$	$u_{\text{GED}}$	Restraint	$k_{\text{h1}}$	$u_{\text{h1}}$
$u_1$	N(12)-H(21)	101.8(5)	7.2(8)	7.2(7)	0.4	7.2
$u_2$	C(6)-H(13)	110.1(2)	4.1(2)	7.6(4)	0.4	7.6
$u_3$	C(9)-H(16)	110.1(2)	4.1 (Tied to $u_2$ )	—	0.4	7.6
$u_4$	C(9)-H(15)	110.1(2)	4.1 (Tied to $u_2$ )	—	0.4	7.7
$u_5$	C(6)-H(14)	110.1(2)	4.1 (Tied to $u_2$ )	—	0.4	7.7
$u_6$	C(1)-H(5)	110.1(2)	4.1 (Tied to $u_2$ )	—	0.4	7.7
$u_7$	C(3)-H(10)	110.1(2)	4.1 (Tied to $u_2$ )	—	0.4	7.7
$u_8$	C(2)-H(8)	110.1(2)	4.1 (Tied to $u_2$ )	—	0.4	7.7
$u_9$	C(1)-H(4)	110.1(2)	4.1 (Tied to $u_2$ )	—	0.4	7.7
$u_{10}$	C(2)-H(7)	110.1(2)	4.1 (Tied to $u_2$ )	—	0.4	7.7
$u_{11}$	C(3)-H(11)	110.1(2)	4.1 (Tied to $u_2$ )	—	0.4	7.7
$u_{12}$	B(17)-H(20)	120.6(10)	8.8 (10)	8.5(9)	0.5	8.5
$u_{13}$	B(17)-H(18)	120.6(10)	8.8 (Tied to $u_{12}$ )	—	0.5	8.5
$u_{14}$	B(17)-H(19)	120.6(10)	8.8 (Tied to $u_{12}$ )	—	0.5	8.6
$u_{15}$	C(6)-N(12)	148.3(2)	4.0 (5)	5.0(5)	0.1	5.0
$u_{16}$	C(9)-N(12)	148.3(2)	4.0 (Tied to $u_{15}$ )	—	0.1	5.0
$u_{17}$	C(2)-C(6)	152.7(4)	4.5 (5)	5.1(5)	0.1	5.1
$u_{18}$	C(3)-C(9)	152.7(4)	4.5 (Tied to $u_{17}$ )	—	0.1	5.1
$u_{19}$	C(1)-C(3)	152.8(6)	4.5 (5)	5.2(5)	0.2	5.2

$u_{20}$	C(1)-C(2)	152.8(6)	4.5 (Tied to $u_{19}$ )	—	0.2	5.2
$u_{21}$	N(12)-B(17)	163.6(3)	5.5 (7)	6.3(6)	0.3	6.3
$u_{22}$	H(10)...H(11)	175.7(4)	12.4 (Fixed)	—	0.1	12.4
$u_{23}$	H(7)...H(8)	175.7(4)	12.4 (Fixed)	—	0.1	12.4
$u_{24}$	H(4)...H(5)	175.7(3)	12.4 (Fixed)	—	0.1	12.4
$u_{25}$	H(15)...H(16)	176.6(4)	12.3 (Fixed)	—	0.1	12.3
$u_{26}$	H(13)...H(14)	176.6(4)	12.3 (Fixed)	—	0.1	12.3
$u_{27}$	H(18)...H(20)	200.8(17)	13.6 (Fixed)	—	0.1	13.6
$u_{28}$	H(19)...H(20)	200.8(17)	13.7 (Fixed)	—	0.1	13.7
$u_{29}$	H(18)...H(19)	200.8(17)	13.7 (Fixed)	—	0.1	13.7
$u_{30}$	C(9)...H(21)	203.9(5)	9.7 (12)	10.4(10)	-0.2	10.4
$u_{31}$	C(6)...H(21)	203.9(5)	9.7 (Tied to $u_{30}$ )	—	-0.2	10.4
$u_{32}$	N(12)...H(14)	206.5(6)	9.3 (8)	10.4(10)	-0.2	10.4
$u_{33}$	N(12)...H(15)	206.5(6)	9.3 (Tied to $u_{32}$ )	—	-0.2	10.4
$u_{34}$	N(12)...H(16)	208.0(6)	9.3 (Tied to $u_{32}$ )	—	-0.1	10.4
$u_{35}$	N(12)...H(13)	208.0(6)	9.3 (Tied to $u_{32}$ )	—	-0.1	10.4
$u_{36}$	C(9)...H(10)	214.3(5)	10.9 (Fixed)	—	-0.1	10.9
$u_{37}$	C(6)...H(8)	214.3(5)	10.9 (Fixed)	—	-0.1	10.9
$u_{38}$	B(17)...H(21)	213.5(5)	12.0 (Fixed)	—	0.1	12.0
$u_{39}$	C(6)...H(7)	214.8(5)	10.8 (Fixed)	—	-0.2	10.8
$u_{40}$	C(9)...H(11)	214.8(5)	10.8 (Fixed)	—	-0.2	10.8
$u_{41}$	C(3)...H(4)	216.8(8)	10.9 (6)	—	-0.1	10.8

$u_{42}$	C(2)...H(4)	216.8(8)	10.9 (Tied to $u_{41}$ )	—	-0.1	10.8
$u_{43}$	C(1)...H(11)	218.0(10)	10.9 (Tied to $u_{41}$ )	—	-0.1	10.9
$u_{44}$	C(1)...H(7)	218.0(10)	10.9 (Tied to $u_{41}$ )	—	-0.1	10.9
$u_{45}$	C(3)...H(5)	216.0(5)	10.8 (Tied to $u_{41}$ )	—	-0.1	10.8
$u_{46}$	C(2)...H(5)	216.0(5)	10.8 (Tied to $u_{41}$ )	—	-0.1	10.8
$u_{47}$	C(1)...H(10)	218.0(9)	10.8 (Fixed)	—	-0.1	10.8
$u_{48}$	C(1)...H(8)	218.0(9)	10.8 (Fixed)	—	-0.1	10.8
$u_{49}$	C(2)...H(14)	215.4(7)	10.8 (Tied to $u_{41}$ )	—	-0.1	10.8
$u_{50}$	C(3)...H(15)	215.4(7)	10.8 (Tied to $u_{41}$ )	—	-0.1	10.8
$u_{51}$	C(3)...H(16)	219.2(7)	10.7 (Fixed)	—	0.0	10.7
$u_{52}$	C(2)...H(13)	219.2(7)	10.7 (Fixed)	—	0.0	10.7
$u_{53}$	N(12)...H(18)	227.0(8)	11.0 (13)	11.9(12)	-0.2	11.9
$u_{54}$	N(12)...H(20)	227.0(8)	11.0 (Tied to $u_{53}$ )	—	-0.2	11.9
$u_{55}$	N(12)...H(19)	227.0(8)	11.0 (Tied to $u_{53}$ )	—	-0.2	11.9
$u_{56}$	H(16)...H(21)	234.3(7)	16.8 (Fixed)	—	0.0	16.8
$u_{57}$	H(13)...H(21)	234.3(7)	16.8 (Fixed)	—	0.0	16.8
$u_{58}$	H(16)...H(20)	243.8(9)	24.4 (Fixed)	—	3.3	24.4
$u_{59}$	H(13)...H(18)	243.8(9)	24.4 (Fixed)	—	3.3	24.4
$u_{60}$	C(6)...C(9)	243.7(5)	7.2 (8)	7.0(7)	-0.2	7.0
$u_{61}$	H(14)...H(15)	242.4(17)	23.9 (Fixed)	—	0.7	23.9
$u_{62}$	H(5)...H(11)	247.2(9)	17.6 (Fixed)	—	0.0	17.6
$u_{63}$	H(5)...H(7)	247.2(9)	17.6 (Fixed)	—	0.0	17.6

$u_{64}$	H(4)...H(8)	249.6(10)	17.6 (Fixed)	—	0.1	17.6
$u_{65}$	H(4)...H(10)	249.6(10)	17.6 (Fixed)	—	0.1	17.6
$u_{66}$	H(18)...H(21)	248.5(9)	17.7 (Fixed)	—	0.0	17.7
$u_{67}$	H(20)...H(21)	248.5(9)	17.7 (Fixed)	—	0.0	17.7
$u_{68}$	H(7)...H(13)	246.0(7)	20.5 (Fixed)	—	0.2	20.5
$u_{69}$	H(11)...H(16)	246.0(7)	20.5 (Fixed)	—	0.2	20.5
$u_{70}$	H(10)...H(15)	249.8(11)	17.6 (Fixed)	—	0.0	17.6
$u_{71}$	H(8)...H(14)	249.8(11)	17.6 (Fixed)	—	0.0	17.6
$u_{72}$	C(2)...N(12)	248.7(5)	7.6 (6)	6.9(7)	-0.3	6.9
$u_{73}$	C(3)...N(12)	248.7(5)	7.6 (Tied to $u_{72}$ )	—	-0.3	6.9
$u_{74}$	C(2)...C(3)	250.5(9)	27.7 (Fixed)	—	2.4	27.7
$u_{75}$	C(1)...C(9)	250.5(9)	27.7 (Fixed)	—	2.4	27.7
$u_{76}$	C(1)...C(6)	246.8(10)	7.6 (8)	7.2(7)	-0.2	7.2
$u_{77}$	H(8)...H(13)	250.4(5)	7.6 (7)	7.1(7)	-0.2	7.1
$u_{78}$	H(10)...H(16)	250.4(5)	7.6 (Tied to $u_{77}$ )	—	-0.2	7.1
$u_{79}$	H(15)...H(19)	252.3(9)	16.5 (Fixed)	—	0.2	16.5
$u_{80}$	H(14)...H(19)	252.3(9)	16.5 (Fixed)	—	0.2	16.5
$u_{81}$	H(5)...H(8)	250.1(9)	16.5 (Fixed)	—	0.2	16.5
$u_{82}$	H(5)...H(10)	250.1(9)	16.5 (Fixed)	—	0.2	16.5
$u_{83}$	H(7)...H(21)	254.6(12)	24.7 (Fixed)	—	0.7	24.7
$u_{84}$	H(11)...H(21)	254.6(12)	24.7 (Fixed)	—	0.7	24.7
$u_{85}$	C(9)...B(17)	258.5(3)	7.3 (6)	8.6(9)	0.0	8.6



$u_{86}$	C(6)...B(17)	258.5(3)	7.3 (Tied to $u_{85}$ )	—	0.0	8.6
$u_{87}$	H(4)...H(14)	259.5(15)	25.6 (Fixed)	—	0.6	25.6
$u_{88}$	H(4)...H(15)	259.5(15)	25.6 (Fixed)	—	0.6	25.6
$u_{89}$	H(7)...H(11)	258.3(17)	25.7 (Fixed)	—	0.8	25.7
$u_{90}$	C(9)...H(14)	266.4(9)	15.7 (Fixed)	—	-0.4	15.7
$u_{91}$	C(6)...H(15)	266.4(9)	15.7 (Fixed)	—	-0.4	15.7
$u_{92}$	C(3)...H(21)	268.7(10)	15.9 (Fixed)	—	-0.3	15.9
$u_{93}$	C(2)...H(21)	268.7(10)	15.9 (Fixed)	—	-0.3	15.9
$u_{94}$	H(16)...B(17)	271.1(8)	15.7 (Fixed)	—	0.4	15.7
$u_{95}$	H(13)...B(17)	271.1(8)	15.7 (Fixed)	—	0.4	15.7
$u_{96}$	H(14)...B(17)	273.7(8)	16.9 (Fixed)	—	0.0	16.9
$u_{97}$	H(15)...B(17)	273.7(8)	16.9 (Fixed)	—	0.0	16.9
$u_{98}$	H(11)...N(12)	276.6(7)	16.3 (Fixed)	—	-0.4	16.3
$u_{99}$	H(7)...N(12)	276.6(7)	16.3 (Fixed)	—	-0.4	16.3
$u_{100}$	C(2)...H(11)	275.1(12)	16.6 (Fixed)	—	-0.3	16.6
$u_{101}$	C(3)...H(7)	275.1(12)	16.6 (Fixed)	—	-0.3	16.6
$u_{102}$	H(4)...C(6)	277.9(4)	16.3 (Fixed)	—	-0.3	16.3
$u_{103}$	H(4)...C(9)	277.9(4)	16.3 (Fixed)	—	-0.3	16.3
$u_{104}$	C(1)...H(15)	279.1(6)	18.2 (Fixed)	—	0.4	18.2
$u_{105}$	C(1)...H(14)	279.1(6)	18.2 (Fixed)	—	0.4	18.2
$u_{106}$	C(9)...H(20)	276.7(16)	16.6 (Fixed)	—	-0.3	16.6
$u_{107}$	C(6)...H(18)	276.7(16)	16.6 (Fixed)	—	-0.3	16.6

$u_{108}$	C(6)...H(19)	283.0(6)	20.1 (Fixed)	—	-0.1	20.1
$u_{109}$	C(9)...H(19)	283.0(6)	20.1 (Fixed)	—	-0.1	20.1
$u_{110}$	C(2)...C(9)	288.5(3)	8.2 (4)	7.5(8)	-0.4	7.5
$u_{111}$	C(3)...C(6)	288.5(3)	8.2 (Tied to $u_{110}$ )	—	-0.4	7.5
$u_{112}$	H(14)...H(21)	289.8(6)	12.2 (Fixed)	—	-1.3	12.2
$u_{113}$	H(15)...H(21)	289.8(6)	12.2 (Fixed)	—	-1.3	12.2
$u_{114}$	C(1)...N(12)	293.6(3)	8.5 (5)	7.5(8)	-0.4	7.5
$u_{115}$	H(4)...H(11)	307.8(11)	12.6 (Fixed)	—	-1.2	12.6
$u_{116}$	H(4)...H(7)	307.8(11)	12.6 (Fixed)	—	-1.2	12.6
$u_{117}$	H(7)...H(14)	306.4(7)	12.6 (Fixed)	—	-1.2	12.6
$u_{118}$	H(11)...H(15)	306.4(7)	12.6 (Fixed)	—	-1.2	12.6
$u_{119}$	H(19)...H(21)	306.7(10)	13.6 (Fixed)	—	-2.0	13.6
$u_{120}$	H(14)...H(18)	307.4(8)	27.5 (Fixed)	—	-0.9	27.5
$u_{121}$	H(15)...H(20)	307.4(8)	27.5 (Fixed)	—	-0.9	27.5
$u_{122}$	H(16)...H(19)	308.0(8)	28.6 (Fixed)	—	-0.9	28.6
$u_{123}$	H(13)...H(19)	308.0(8)	28.6 (Fixed)	—	-0.9	28.6
$u_{124}$	C(1)...H(21)	327.1(11)	16.3 (Fixed)	—	-0.8	16.3
$u_{125}$	C(2)...H(15)	327.2(7)	16.5 (Fixed)	—	-0.9	16.5
$u_{126}$	C(3)...H(14)	327.2(7)	16.5 (Fixed)	—	-0.9	16.5
$u_{127}$	C(6)...H(11)	329.9(5)	16.4 (Fixed)	—	-0.8	16.4
$u_{128}$	H(7)...C(9)	329.9(5)	16.4 (Fixed)	—	-0.8	16.4
$u_{129}$	H(4)...N(12)	333.3(3)	16.2 (Fixed)	—	-0.8	16.2

$u_{130}$	C(6)...H(16)	335.6(6)	10.2 (Fixed)	—	-1.1	10.2
$u_{131}$	C(9)...H(13)	335.6(6)	10.2 (Fixed)	—	-1.1	10.2
$u_{132}$	H(10)...N(12)	341.3(4)	10.2 (Fixed)	—	-1.1	10.2
$u_{133}$	H(8)...N(12)	341.3(4)	10.2 (Fixed)	—	-1.1	10.2
$u_{134}$	C(3)...H(8)	342.1(10)	10.3 (Fixed)	—	-1.0	10.3
$u_{135}$	C(2)...H(10)	342.1(10)	10.3 (Fixed)	—	-1.0	10.3
$u_{136}$	H(5)...C(9)	345.1(6)	10.3 (Fixed)	—	-1.1	10.3
$u_{137}$	H(5)...C(6)	345.1(6)	10.3 (Fixed)	—	-1.1	10.3
$u_{138}$	C(1)...H(16)	347.1(5)	10.2 (Fixed)	—	-1.0	10.2
$u_{139}$	C(1)...H(13)	347.1(5)	10.2 (Fixed)	—	-1.0	10.2
$u_{140}$	C(6)...H(20)	355.0(9)	11.5 (Fixed)	—	-1.9	11.5
$u_{141}$	C(9)...H(18)	355.0(9)	11.5 (Fixed)	—	-1.9	11.5
$u_{142}$	H(13)...H(15)	362.4(10)	17.3 (Fixed)	—	-1.4	17.3
$u_{143}$	H(14)...H(16)	362.4(10)	17.3 (Fixed)	—	-1.4	17.3
$u_{144}$	H(8)...H(21)	366.9(8)	17.3 (Fixed)	—	-1.4	17.3
$u_{145}$	H(10)...H(21)	366.9(8)	17.3 (Fixed)	—	-1.4	17.3
$u_{146}$	H(16)...H(18)	375.1(13)	17.6 (Fixed)	—	-2.1	17.6
$u_{147}$	H(13)...H(20)	375.1(13)	17.6 (Fixed)	—	-2.1	17.6
$u_{148}$	H(8)...H(11)	375.4(13)	18.0 (Fixed)	—	-1.4	18.0
$u_{149}$	H(7)...H(10)	375.4(13)	18.0 (Fixed)	—	-1.4	18.0
$u_{150}$	H(4)...H(13)	378.8(6)	17.9 (Fixed)	—	-1.4	17.9
$u_{151}$	H(4)...H(16)	378.8(6)	17.9 (Fixed)	—	-1.4	17.9

$u_{152}$	H(5)...H(15)	377.1(17)	18.0 (Fixed)	—	-1.4	18.0
$u_{153}$	H(5)...H(14)	377.1(17)	18.0 (Fixed)	—	-1.4	18.0
$u_{154}$	H(14)...H(20)	378.4(12)	18.5 (Fixed)	—	-2.5	18.5
$u_{155}$	H(15)...H(18)	378.4(12)	18.5 (Fixed)	—	-2.5	18.5
$u_{156}$	C(6)...H(10)	386.5(3)	11.1 (Fixed)	—	-1.5	11.1
$u_{157}$	H(8)...C(9)	386.5(3)	11.1 (Fixed)	—	-1.5	11.1
$u_{158}$	C(2)...H(16)	387.0(4)	10.9 (Fixed)	—	-1.4	10.9
$u_{159}$	C(3)...H(13)	387.0(4)	10.9 (Fixed)	—	-1.4	10.9
$u_{160}$	H(5)...N(12)	392.3(10)	17.9 (Fixed)	—	-1.9	17.9
$u_{161}$	H(4)...H(21)	392.1(4)	11.1 (Fixed)	—	-1.4	11.1
$u_{162}$	C(2)...B(17)	395.0(4)	9.0 (3)	8.6(9)	-0.8	8.6
$u_{163}$	C(3)...B(17)	395.0(4)	11.8 (Tied to $u_{162}$ )	—	-0.8	8.6
$u_{164}$	H(7)...H(15)	395.3(7)	18.0 (Fixed)	—	-1.9	18.0
$u_{165}$	H(11)...H(14)	395.3(7)	18.0 (Fixed)	—	-1.9	18.0
$u_{166}$	H(5)...H(21)	409.0(12)	21.2 (Fixed)	—	-1.5	21.2
$u_{167}$	H(8)...H(15)	406.5(7)	21.8 (Fixed)	—	-1.7	21.8
$u_{168}$	H(10)...H(14)	406.5(7)	21.8 (Fixed)	—	-1.7	21.8
$u_{169}$	H(11)...H(13)	410.2(6)	21.6 (Fixed)	—	-1.6	21.6
$u_{170}$	H(7)...H(16)	410.2(6)	21.6 (Fixed)	—	-1.6	21.6
$u_{171}$	H(13)...H(16)	413.5(11)	13.8 (Fixed)	—	-1.8	13.8
$u_{172}$	C(2)...H(18)	419.7(7)	17.7 (Fixed)	—	-0.8	17.7
$u_{173}$	C(3)...H(20)	419.7(7)	17.7 (Fixed)	—	-0.8	17.7

$u_{174}$	C(3)...H(19)	424.2(7)	18.8 (Fixed)	—	-1.4	18.8
$u_{175}$	C(2)...H(19)	424.2(7)	18.8 (Fixed)	—	-1.4	18.8
$u_{176}$	H(11)...B(17)	425.8(9)	17.5 (Fixed)	—	-1.1	17.5
$u_{177}$	H(7)...B(17)	425.8(9)	17.5 (Fixed)	—	-1.1	17.5
$u_{178}$	H(8)...H(10)	426.1(13)	13.9 (Fixed)	—	-1.9	13.9
$u_{179}$	H(5)...H(13)	430.9(6)	13.9 (Fixed)	—	-1.8	13.9
$u_{180}$	H(5)...H(16)	430.9(6)	13.9 (Fixed)	—	-1.8	13.9
$u_{181}$	H(7)...H(18)	436.3(12)	24.5 (Fixed)	—	-0.5	24.5
$u_{182}$	H(11)...H(20)	436.3(12)	24.5 (Fixed)	—	-0.5	24.5
$u_{183}$	C(1)...B(17)	445.6(6)	12.6 (7)	9.4(9)	-1.2	9.4
$u_{184}$	H(4)...H(19)	448.0(17)	31.2 (Fixed)	—	-0.2	31.2
$u_{185}$	C(1)...H(19)	458.6(13)	20.2 (Fixed)	—	-1.3	20.2
$u_{186}$	H(4)...B(17)	463.4(9)	21.1 (Fixed)	—	-1.5	21.1
$u_{187}$	H(8)...B(17)	471.4(5)	13.1 (Fixed)	—	-1.7	13.1
$u_{188}$	H(10)...B(17)	471.4(5)	13.1 (Fixed)	—	-1.7	13.1
$u_{189}$	C(2)...H(20)	473.9(9)	13.2 (Fixed)	—	-2.4	13.2
$u_{190}$	C(3)...H(18)	473.9(9)	13.2 (Fixed)	—	-2.4	13.2
$u_{191}$	H(8)...H(18)	482.1(7)	22.1 (Fixed)	—	-1.2	22.1
$u_{192}$	H(10)...H(20)	482.1(7)	22.1 (Fixed)	—	-1.2	22.1
$u_{193}$	H(11)...H(19)	480.2(8)	20.5 (Fixed)	—	-2.9	20.5
$u_{194}$	H(7)...H(19)	480.2(8)	20.5 (Fixed)	—	-2.9	20.5
$u_{195}$	H(8)...H(19)	486.3(8)	25.1 (Fixed)	—	-1.9	25.1

<i>u</i> <sub>196</sub>	H(10)...H(19)	486.3(8)	25.1 (Fixed)	—	-1.9	25.1
<i>u</i> <sub>197</sub>	H(10)...H(13)	489.1(4)	12.8 (Fixed)	—	-2.8	12.8
<i>u</i> <sub>198</sub>	H(8)...H(16)	489.1(4)	12.8 (Fixed)	—	-2.8	12.8
<i>u</i> <sub>199</sub>	H(7)...H(20)	491.0(12)	23.2 (Fixed)	—	-2.3	23.2
<i>u</i> <sub>200</sub>	H(11)...H(18)	491.0(12)	23.2 (Fixed)	—	-2.3	23.2
<i>u</i> <sub>201</sub>	C(1)...H(18)	504.2(8)	15.4 (Fixed)	—	-2.3	15.4
<i>u</i> <sub>202</sub>	C(1)...H(20)	504.2(8)	15.4 (Fixed)	—	-2.3	15.4
<i>u</i> <sub>203</sub>	H(4)...H(20)	529.6(10)	24.2 (Fixed)	—	-3.1	24.2
<i>u</i> <sub>204</sub>	H(4)...H(18)	529.6(10)	24.2 (Fixed)	—	-3.1	24.2
<i>u</i> <sub>205</sub>	H(5)...B(17)	548.9(6)	11.5 (Fixed)	—	-2.5	11.5
<i>u</i> <sub>206</sub>	H(10)...H(18)	562.1(9)	15.0 (Fixed)	—	-4.0	15.0
<i>u</i> <sub>207</sub>	H(8)...H(20)	562.1(9)	15.0 (Fixed)	—	-4.0	15.0
<i>u</i> <sub>208</sub>	H(5)...H(19)	566.5(13)	21.0 (Fixed)	—	-3.0	21.0
<i>u</i> <sub>209</sub>	H(5)...H(18)	602.4(7)	17.8 (Fixed)	—	-3.6	17.8
<i>u</i> <sub>210</sub>	H(5)...H(20)	602.4(7)	17.8 (Fixed)	—	-3.6	17.8

---

<sup>a</sup> All values are tabulated in pm.

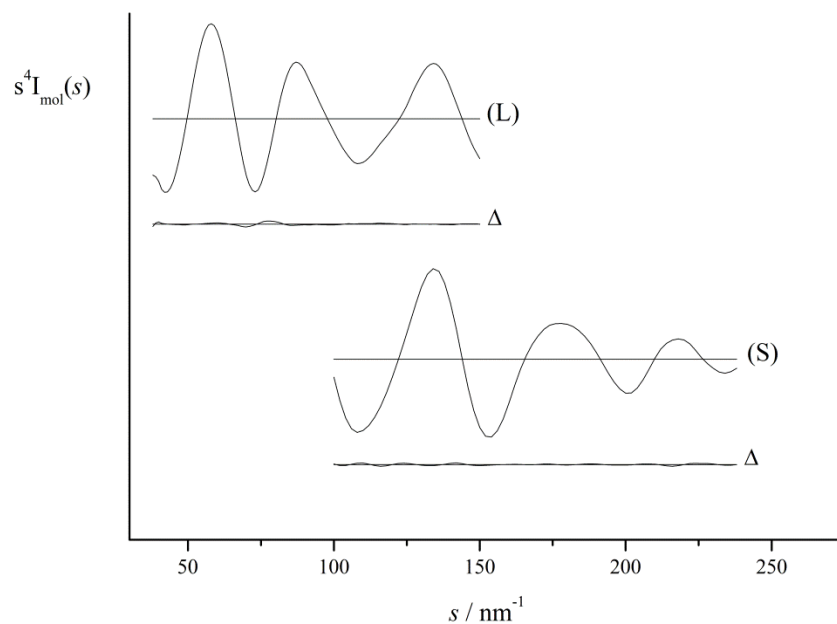


Figure S1: Experimental and final weighted difference (experimental – theoretical) MICs for **PYB**. L indicates data from the long nozzle-to-camera distance, S indicates data from the short nozzle-to-camera distance.

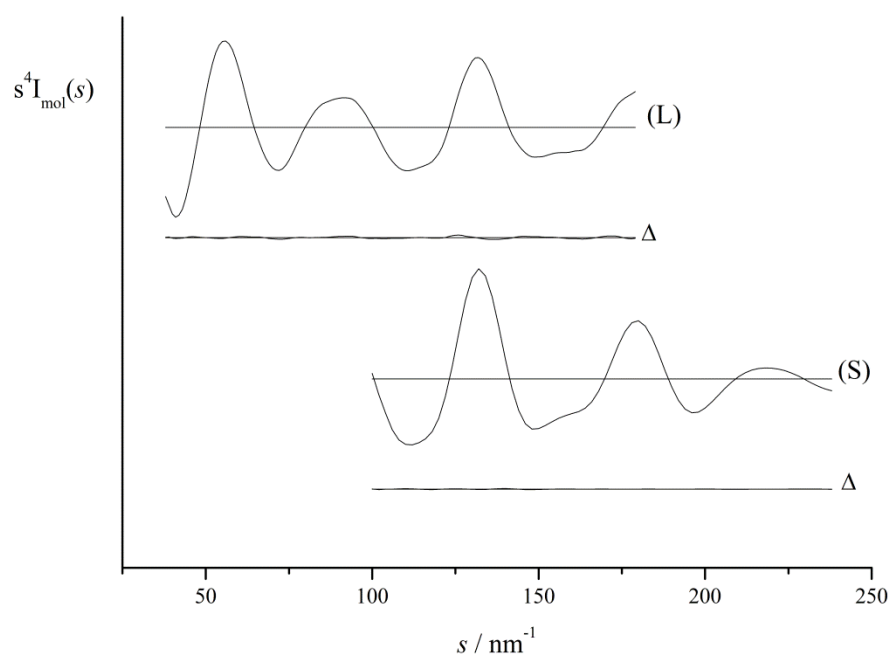


Figure S2: Experimental and final weighted difference (experimental – theoretical) MICs for **PIB**. L indicates data from the long nozzle-to-camera distance, S indicates data from the short nozzle-to-camera distance.

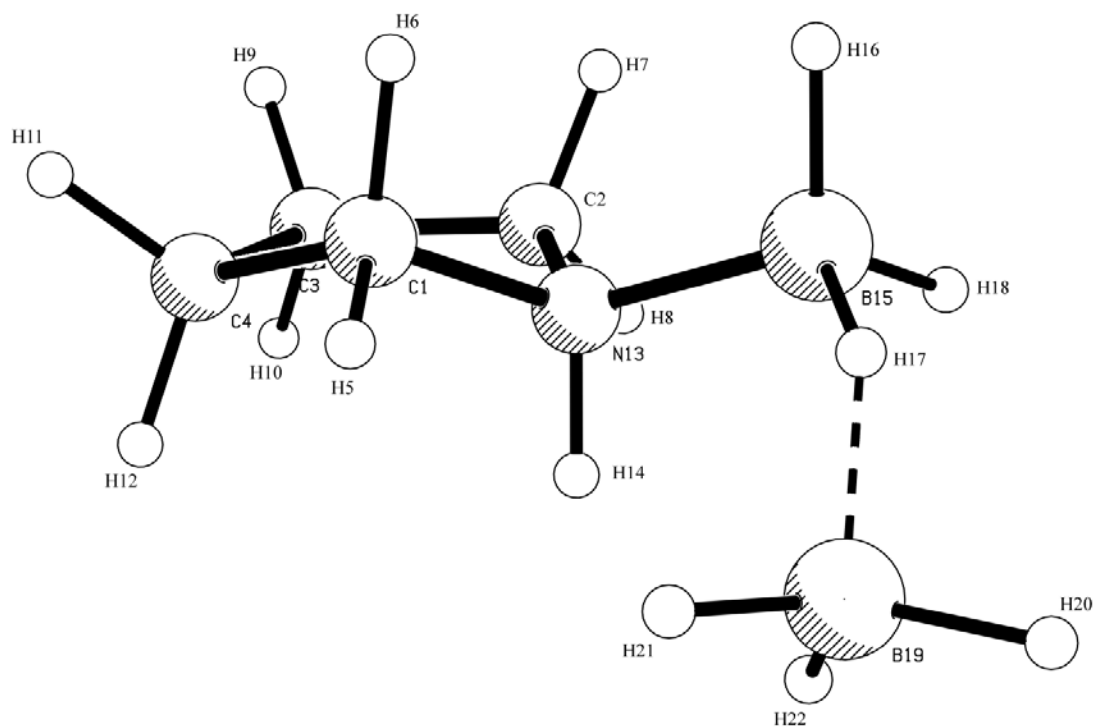


Figure S3: The optimized structure of the condensation product formed between **PYB** and **BH<sub>3</sub>** (**PYB...BH<sub>3</sub>**)

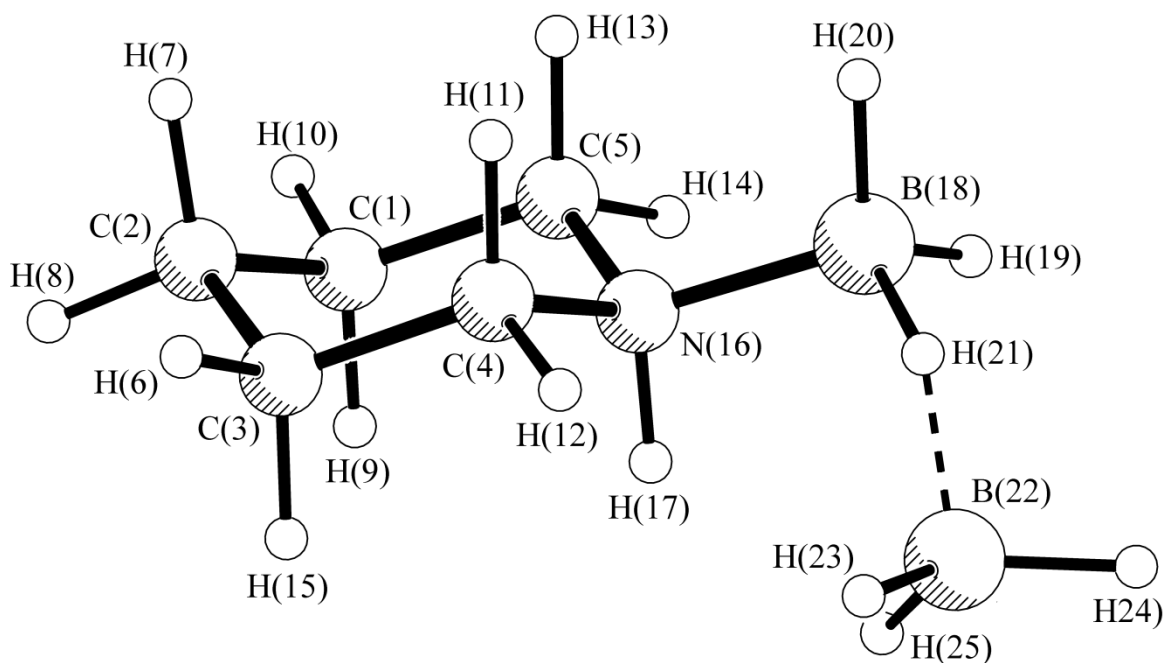


Figure S4: The optimized structure of the condensation product formed between **PIB** and **BH<sub>3</sub>** (**PIB...BH<sub>3</sub>**)



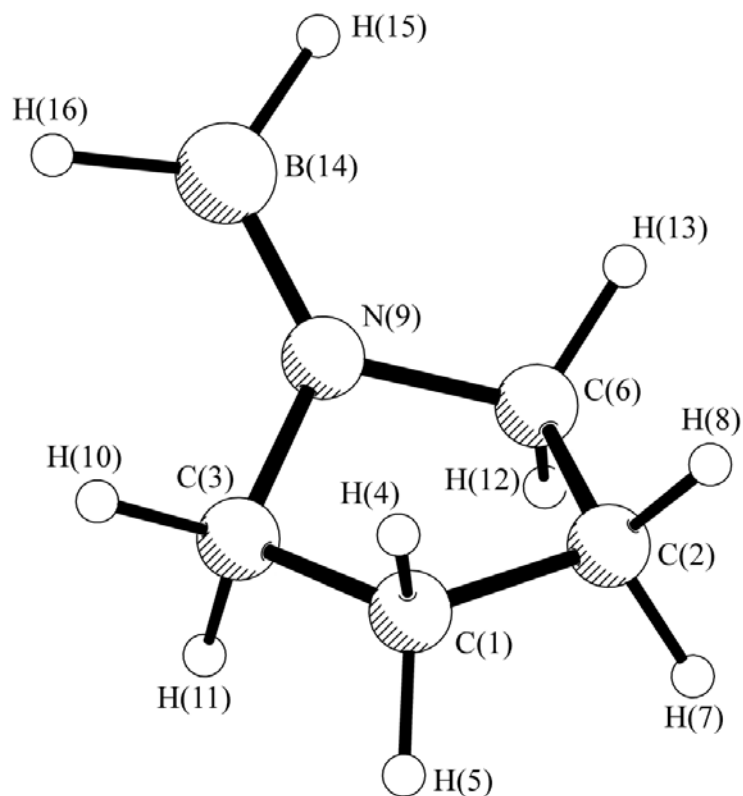


Figure S5: The lowest-energy ground state structure of **D-PYB** showing the atom numbering.

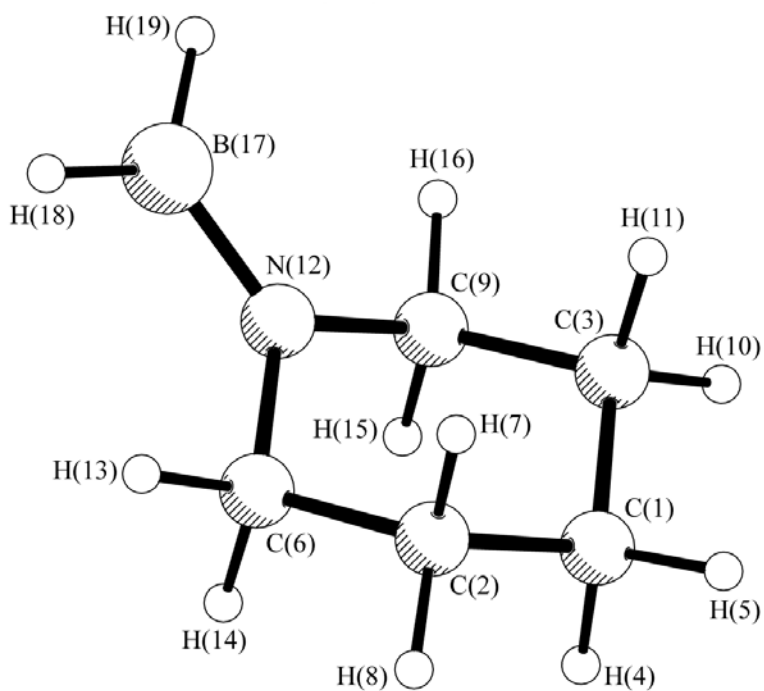


Figure S6: The lowest-energy ground state structure of **D-PIB** showing the atom numbering.

## Supplementary Information Part II:

### Data for refinement of PYB and PIB using models based on MP2 optimized geometries

Table S24: Calculated coordinates at the MP2/6-31G\* level for **PYB**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-1.49405	-0.77470	-0.08698
C	-1.51197	0.76570	0.05806
C	-0.04352	-1.15695	0.19760
H	-1.76421	-1.06858	-1.10678
H	-2.19306	-1.27277	0.58971
C	-0.02740	1.18117	0.08351
H	-2.00945	1.07581	0.98048
H	-2.04887	1.23533	-0.77037
N	0.74716	-0.01965	-0.33798
H	0.29433	-2.08751	-0.26211
H	0.17234	-1.19876	1.26846
H	0.31753	1.41767	1.09225
H	0.22621	2.01927	-0.56788
B	2.32607	-0.00142	0.09239
H	2.31502	0.04161	1.30557
H	2.78397	0.99577	-0.42349
H	2.78910	-1.02935	-0.35409
H	0.71832	-0.07513	-1.36095

Table S25: Calculated coordinates at the MP2/6-311G\* level for **PYB**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-1.49575	-0.77542	-0.08451
C	-1.51249	0.76786	0.05254
C	-0.04221	-1.15617	0.19611
H	-1.77331	-1.07602	-1.09962
H	-2.18847	-1.26749	0.60166
C	-0.02577	1.17877	0.08801
H	-2.01586	1.08312	0.96901
H	-2.03957	1.23433	-0.78302
N	0.74863	-0.01930	-0.33770
H	0.29397	-2.08554	-0.26585
H	0.17326	-1.20128	1.26635
H	0.31274	1.40806	1.09992
H	0.23271	2.02053	-0.55567
B	2.32012	-0.00151	0.08969
H	2.32147	0.03703	1.30485
H	2.78503	0.99866	-0.42022
H	2.79284	-1.02703	-0.35897
H	0.72154	-0.07195	-1.35582

Table S26: Calculated coordinates at the MP2/6-311+G\* level for **PYB**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-1.49235	-0.77032	-0.10867
C	-1.51017	0.76185	0.09849
C	-0.04889	-1.15558	0.20236
H	-1.72958	-1.02366	-1.14748
H	-2.21096	-1.29240	0.52741
C	-0.02537	1.18656	0.04403
H	-1.94082	1.02101	1.06858
H	-2.10678	1.26547	-0.66564
N	0.75051	-0.02833	-0.33993
H	0.29269	-2.09219	-0.24119
H	0.14855	-1.18556	1.27742
H	0.35414	1.48962	1.02145
H	0.19356	1.98563	-0.66575
B	2.31619	-0.00232	0.10914
H	2.29569	0.06402	1.32413
H	2.79128	0.98680	-0.41524
H	2.79626	-1.03845	-0.30924
H	0.74211	-0.10550	-1.35788

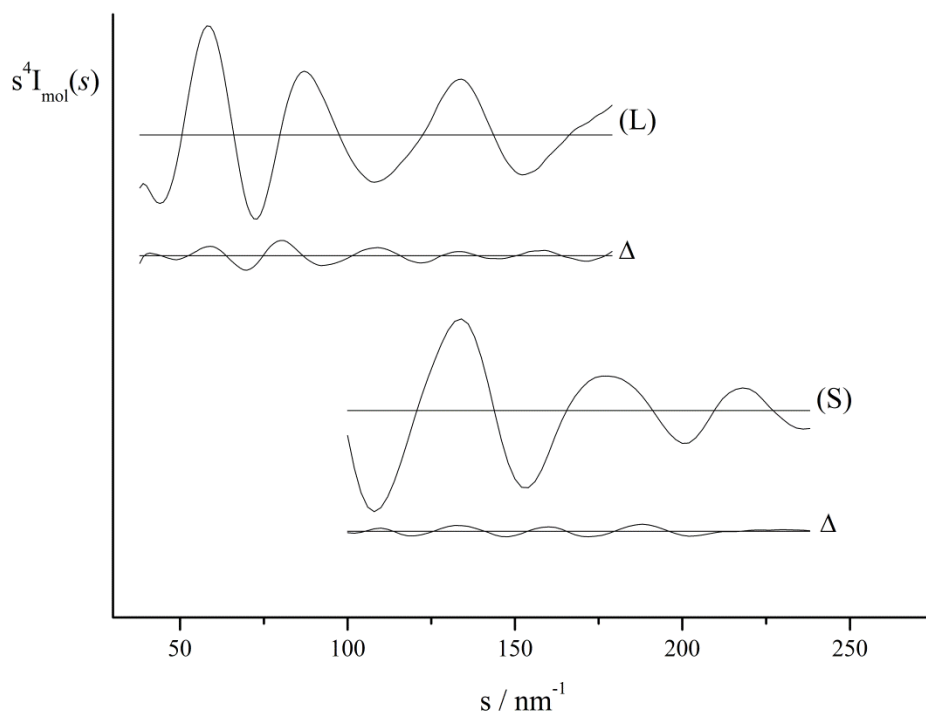


Figure S7: Experimental and final weighted difference (experimental – theoretical) MICs for **PYB** using the MP2 starting structure, vibrational corrections and restraints. L indicates data from the long nozzle-to-camera distance, S indicates data from the short nozzle-to-camera distance.

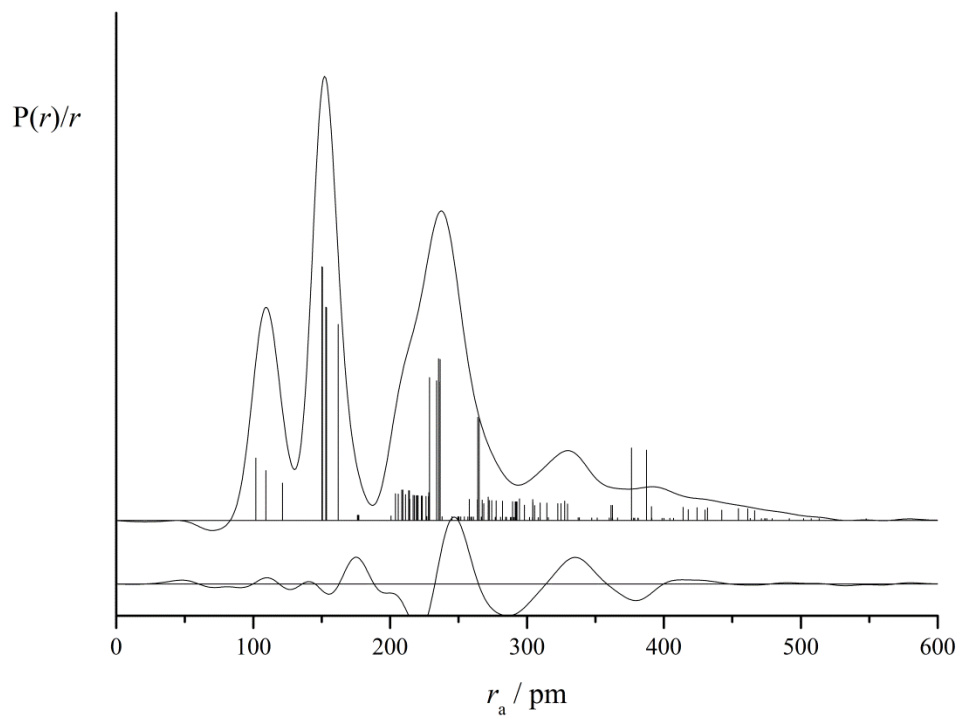


Figure 8: Experimental and difference (experimental minus theoretical) RDCs for the GED refinement of **PYB** using the MP2 starting structure, vibrational corrections and restraints. Before Fourier inversion, the data were multiplied by  $s \cdot \exp(-0.00002s^2)/(Z_C - f_C)(Z_N - f_N)$ .

Table S27: Least-squares correlation matrix<sup>a</sup> ( $\times 100$ ) for the refinement of **PIB** (using MP2/6-311+G\* model).

	<i>p</i> <sub>20</sub>	<i>u</i> <sub>7</sub>	<i>u</i> <sub>10</sub>	<i>u</i> <sub>22</sub>	<i>u</i> <sub>43</sub>	<i>k</i> <sub>1</sub>	<i>k</i> <sub>2</sub>
<i>p</i> <sub>2</sub>			-51				
<i>p</i> <sub>7</sub>		66					
<i>p</i> <sub>12</sub>	-50						
<i>u</i> <sub>9</sub>			-57				
<i>u</i> <sub>20</sub>				-66			
<i>u</i> <sub>41</sub>					-57		
<i>u</i> <sub>6</sub>						71	
<i>k</i> <sub>1</sub>							59

<sup>a</sup> Only values  $\geq 50\%$  are included in the least-squares correlation matrix. *k*<sub>1</sub> is a scale factor

Table S28: Calculated coordinates at the MP2/6-31G\* level for **PIB**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-0.75953	-1.74923	0.00000
C	-0.09609	-1.17932	1.25296
C	-0.09609	-1.17932	-1.25296
H	-1.82436	-1.48224	0.00000
H	-0.70528	-2.84328	0.00000
C	-0.09609	0.34368	1.22635
H	0.93828	-1.54344	1.32199
H	-0.60944	-1.52123	2.15889
C	-0.09609	0.34368	-1.22635
H	-0.60944	-1.52123	-2.15889
H	0.93828	-1.54344	-1.32199
N	0.54803	0.88516	0.00000
H	0.43139	0.77559	2.07994
H	-1.11489	0.74367	1.23006
H	-1.11489	0.74367	-1.23006
H	0.43139	0.77559	-2.07994
B	0.58903	2.52744	0.00000
H	1.18407	2.82732	1.01316
H	-0.57376	2.87356	0.00000
H	1.18407	2.82732	-1.01316
H	1.52647	0.57784	0.00000



Table S29: Calculated coordinates at the MP2/6-311G\* level for **PIB**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-0.75977	-1.75125	0.00000
C	-0.09565	-1.17957	1.25302
C	-0.09565	-1.17957	-1.25302
H	-1.82450	-1.48585	0.00000
H	-0.70452	-2.84461	0.00000
C	-0.09565	0.34470	1.22392
H	0.93720	-1.54586	1.32632
H	-0.61118	-1.51707	2.15858
C	-0.09565	0.34470	-1.22392
H	-0.61118	-1.51707	-2.15858
H	0.93720	-1.54586	-1.32632
N	0.55007	0.88763	0.00000
H	0.42782	0.77638	2.07925
H	-1.11459	0.74304	1.22661
H	-1.11459	0.74304	-1.22661
H	0.42782	0.77638	-2.07925
B	0.58794	2.52126	0.00000
H	1.18234	2.83192	1.01308
H	-0.57441	2.87561	0.00000
H	1.18234	2.83192	-1.01308
H	1.52436	0.58431	0.00000

Table S30: Calculated coordinates at the MP2/6-311+G\* level for **PIB**.

Atom	x	y	z
C	-1.88916	0.00000	0.27885
C	-1.16336	-1.25220	-0.21363
C	-1.16336	1.25220	-0.21363
H	-1.91451	0.00000	1.37635
H	-2.92989	0.00000	-0.06169
C	0.30770	-1.22333	0.18405
H	-1.24666	-1.32509	-1.30685
H	-1.62381	-2.15865	0.19444
C	0.30770	1.22333	0.18405
H	-1.62381	2.15865	0.19444
H	-1.24666	1.32509	-1.30685
N	0.99922	0.00000	-0.29957
H	0.86190	-2.07890	-0.20769
H	0.42783	-1.22564	1.27221
H	0.42783	1.22564	1.27222
H	0.86190	2.07890	-0.20768
B	2.58816	0.00000	0.08180
H	3.04200	-1.01384	-0.41293
H	2.63142	0.00000	1.29765
H	3.04200	1.01384	-0.41293
H	0.95802	0.00000	-1.32080

Table S31: Refined ( $r_{h1}$ ) and calculated ( $r_e$ ) geometric parameters for **PIB**.

Parameter <sup>a</sup>	MP2/6- 311+G* ( $r_e$ )	SARACEN ( $r_{h1}$ )	Restraint
$p_1$ $r_{B-H}$ av	121.6	121.5(4)	121.6(3)
$p_2$ $r_{B-N}$	163.4	163.9(5)	163.4(9)
$p_3$ $r_{N-C}$	148.6	148.6(1)	148.6(1)
$p_4$ $r_{N-H}$	102.2	102.3(6)	102.2(5)
$p_5$ $r_{C-C}$	152.4	152.4(1)	152.4(1)
$p_6$ $r_{C(10)...N(5)}$	294.6	295.9(5)	294.6(5)
$p_7$ $r_{C-H}$ av	109.6	109.5(2)	-
$p_8$ $\angle N-B-H$ av	105.5	105.4(2)	105.5(2)
$p_9$ $\angle C(6)-N(5)-B(1)$	112.1	112.6(2)	112.1(2)
$p_{10}$ $\angle H(11)-N(5)-B(1)$	105.8	105.8(3)	105.8(2)
$p_{11}$ $\angle C(8)-C(6)-N(5)$	112.3	112.2(2)	112.3(2)
$p_{12}$ $\angle C(10)...N(5)-B(1)$	155.2	155.2(3)	155.2(3)
$p_{13}$ av btw $\angle H(12)-C(6)-N(5)$ and $\angle H(13)-C(6)-N(5)$	106.5	106.4(2)	106.5(2)
$p_{14}$ diff btw $\angle H(12)-C(6)-N(5)$ and $\angle H(13)-C(6)-N(5)/2$	0.6	0.6(2)	0.6(2)
$p_{15}$ av btw $\angle H(14)-C(8)-C(6)$ and $\angle H(15)-C(8)-C(6)$	109.2	109.1(2)	109.2(2)
$p_{16}$ diff between $\angle H(14)-C(8)-C(6)$ and $\angle H(15)-C(8)-C(6)/2$	0.3	0.3(2)	0.3(1)
$p_{17}$ av btw $\angle H(20)-C(10)...N(5)$ and $\angle H(21)-C(10)...N(5)$	126.6	126.6(3)	126.6(2)
$p_{18}$ diff btw $\angle H(20)-C(10)...N(5)$ and $\angle H(21)-C(10)p...N(5) /2$	24.0	24.0(3)	24.0(3)
$p_{19}$ $\phi C(6)-N(5)-B(1)-H(2)$	62.7	62.6(2)	62.7(1)
$p_{20}$ $\phi C(8)-C(6)-N(5)-B(1)$	177.9	177.9(3)	177.9(3)

<i>p</i> <sub>21</sub>	∠H(12)-C(6)-N(5)-B(1)	-60.3	-60.3(3)	-60.3(2)
<i>p</i> <sub>22</sub>	∠H(13)-C(6)-N(5)-B(1)	54.1	54.1(3)	54.1(2)
<i>p</i> <sub>23</sub>	∠H(14)-C(8)-C(6)-N(5)	178.4	178.4(3)	178.4(2)
<i>p</i> <sub>24</sub>	∠H(15)-C(8)-C(6)-N(5)	-65.6	-65.6(3)	-65.6(2)

---

<sup>a</sup> Distances in pm and angles in °. Digits in parentheses are the estimated standard deviation of the last digits.

Table S32. Internuclear distances ( $r_a$  / pm), refined ( $u_{\text{GED}}$ ) and theoretical ( $u_{\text{h1}}$ ) amplitudes of vibration and restraints and distance corrections ( $k_{\text{h1}}$ ) for **PIB**.<sup>a</sup>

Amp.	Atomic Pair	$r_a$	$u_{\text{GED}}$	Restraint	$k_{\text{h1}}$	$u_{\text{h1}}$
$u_1$	N(12)-H(21)	102.2(6)	7.2(9)	7.2(7)	0.4	7.2
$u_2$	C(6)-H(13)	109.7(2)	4.6(2)	7.6(8)	0.4	7.6
$u_3$	C(9)-H(16)	109.7(2)	4.6 (Tied to $u_2$ )	—	0.4	7.6
$u_4$	C(9)-H(15)	109.7(2)	4.6 (Tied to $u_2$ )	—	0.4	7.6
$u_5$	C(6)-H(14)	109.7(2)	4.6 (Tied to $u_2$ )	—	0.4	7.6
$u_6$	C(1)-H(5)	109.7(2)	4.6 (Tied to $u_2$ )	—	0.4	7.6
$u_7$	C(3)-H(10)	109.7(2)	4.6 (Tied to $u_2$ )	—	0.4	7.6
$u_8$	C(2)-H(8)	109.7(2)	4.6 (Tied to $u_2$ )	—	0.4	7.6
$u_9$	C(1)-H(4)	109.7(2)	4.6 (Tied to $u_2$ )	—	0.4	7.7
$u_{10}$	C(2)-H(7)	109.7(2)	4.7 (Tied to $u_2$ )	—	0.4	7.7
$u_{11}$	C(3)-H(11)	109.7(2)	4.7 (Tied to $u_2$ )	—	0.4	7.7
$u_{12}$	B(17)-H(20)	121.3(4)	8.9(10)	8.6(9)	0.5	8.6
$u_{13}$	B(17)-H(18)	121.3(4)	8.9 (Tied to $u_{12}$ )	—	0.5	8.6
$u_{14}$	B(17)-H(19)	121.3(4)	8.9 (Tied to $u_{12}$ )	—	0.5	8.6
$u_{15}$	C(6)-N(12)	148.5(1)	4.8(5)	5.0(5)	0.1	5.0
$u_{16}$	C(9)-N(12)	148.5(1)	4.8 (Tied to $u_{15}$ )	—	0.1	5.0
$u_{17}$	C(2)-C(6)	152.4(1)	4.6(3)	5.1(5)	0.1	5.1
$u_{18}$	C(3)-C(9)	152.4(1)	4.6 (Tied to $u_{17}$ )	—	0.1	5.1
$u_{19}$	C(1)-C(3)	152.0(4)	4.6 (Tied to $u_{17}$ )	—	0.2	5.1

$u_{20}$	C(1)-C(2)	152.0(4)	4.6 (Tied to $u_{17}$ )	—	0.2	5.1
$u_{21}$	N(12)-B(17)	164.0(5)	5.4(7)	6.3(9)	0.4	6.3
$u_{22}$	H(10)...H(11)	174.7(5)	12.3 (Fixed)	—	0.1	12.3
$u_{23}$	H(7)...H(8)	174.7(5)	12.3 (Fixed)	—	0.1	12.3
$u_{24}$	H(4)...H(5)	175.0(6)	12.3 (Fixed)	—	0.1	12.3
$u_{25}$	H(15)...H(16)	175.8(5)	12.3 (Fixed)	—	0.1	12.3
$u_{26}$	H(13)...H(14)	175.8(5)	12.3 (Fixed)	—	0.1	12.3
$u_{27}$	H(18)...H(20)	202.0(7)	13.7 (Fixed)	—	0.1	13.7
$u_{28}$	H(19)...H(20)	202.0(7)	13.7 (Fixed)	—	0.1	13.7
$u_{29}$	H(18)...H(19)	202.0(7)	13.7 (Fixed)	—	0.1	13.7
$u_{30}$	C(9)...H(21)	203.8(5)	10.4(7)	10.3(10)	-0.1	10.3
$u_{31}$	C(6)...H(21)	203.8(5)	10.4 (Tied to $u_{30}$ )	—	-0.1	10.3
$u_{32}$	N(12)...H(14)	206.6(4)	10.4 (Tied to $u_{30}$ )	—	-0.1	10.4
$u_{33}$	N(12)...H(15)	206.6(4)	10.4 (Tied to $u_{30}$ )	—	-0.1	10.4
$u_{34}$	N(12)...H(16)	208.1(4)	10.4 (Tied to $u_{30}$ )	—	-0.1	10.4
$u_{35}$	N(12)...H(13)	208.1(4)	10.4 (Tied to $u_{30}$ )	—	-0.1	10.4
$u_{36}$	C(9)...H(10)	213.7(4)	11.9(3)	10.8(10)	-0.1	10.8
$u_{37}$	C(6)...H(8)	213.7(4)	11.9 (Tied to $u_{36}$ )	—	-0.1	10.8
$u_{38}$	B(17)...H(21)	214.8(7)	13.1 (Tied to $u_{36}$ )	—	0.1	11.9
$u_{39}$	C(6)...H(7)	214.4(4)	11.8 (Tied to $u_{36}$ )	—	-0.1	10.7
$u_{40}$	C(9)...H(11)	214.4(4)	11.8 (Tied to $u_{36}$ )	—	-0.1	10.7
$u_{41}$	C(3)...H(4)	214.9(7)	11.8 (Tied to $u_{36}$ )	—	-0.1	10.7

$u_{42}$	C(2)...H(4)	214.9(7)	11.8 (Tied to $u_{36}$ )	—	-0.1	10.7
$u_{43}$	C(1)...H(11)	215.6(9)	11.8 (Tied to $u_{36}$ )	—	-0.1	10.8
$u_{44}$	C(1)...H(7)	215.6(9)	11.8 (Tied to $u_{36}$ )	—	-0.1	10.8
$u_{45}$	C(3)...H(5)	215.8(5)	11.8 (Tied to $u_{36}$ )	—	-0.1	10.7
$u_{46}$	C(2)...H(5)	215.8(5)	11.8 (Tied to $u_{36}$ )	—	-0.1	10.7
$u_{47}$	C(1)...H(10)	214.7(6)	11.8 (Tied to $u_{36}$ )	—	0.0	10.7
$u_{48}$	C(1)...H(8)	214.7(6)	11.8 (Tied to $u_{36}$ )	—	0.0	10.7
$u_{49}$	C(2)...H(14)	217.2(5)	11.8 (Tied to $u_{36}$ )	—	-0.1	10.7
$u_{50}$	C(3)...H(15)	217.2(5)	11.8 (Tied to $u_{36}$ )	—	-0.1	10.7
$u_{51}$	C(3)...H(16)	218.4(5)	11.6 (Tied to $u_{36}$ )	—	0.0	10.6
$u_{52}$	C(2)...H(13)	218.4(5)	11.6 (Tied to $u_{36}$ )	—	0.0	10.6
$u_{53}$	N(12)...H(18)	227.7(7)	11.2(12)	11.9(10)	-0.2	11.9
$u_{54}$	N(12)...H(20)	227.7(7)	11.2 (Tied to $u_{53}$ )	—	-0.2	11.9
$u_{55}$	N(12)...H(19)	227.7(7)	11.2 (Tied to $u_{53}$ )	—	-0.2	11.9
$u_{56}$	H(16)...H(21)	234.9(6)	16.7 (Fixed)	—	0.0	16.7
$u_{57}$	H(13)...H(21)	234.9(6)	16.7 (Fixed)	—	0.0	16.7
$u_{58}$	H(16)...H(20)	245.8(9)	24.1 (Fixed)	—	3.4	24.1
$u_{59}$	H(13)...H(18)	245.8(9)	24.1 (Fixed)	—	3.4	24.1
$u_{60}$	C(6)...C(9)	243.1(4)	7.6(8)	7.0(7)	-0.2	7.0
$u_{61}$	H(14)...H(15)	242.3(14)	24.0 (Fixed)	—	0.7	24.0
$u_{62}$	H(5)...H(11)	247.1(11)	17.5 (Fixed)	—	0.1	17.5
$u_{63}$	H(5)...H(7)	247.1(11)	17.5 (Fixed)	—	0.1	17.5

$u_{64}$	H(4)...H(8)	245.2(7)	17.5 (Fixed)	—	0.1	17.5
$u_{65}$	H(4)...H(10)	245.2(7)	17.5 (Fixed)	—	0.1	17.5
$u_{66}$	H(18)...H(21)	247.5(8)	20.6 (Fixed)	—	0.2	20.6
$u_{67}$	H(20)...H(21)	247.5(8)	20.6 (Fixed)	—	0.2	20.6
$u_{68}$	H(7)...H(13)	248.1(8)	17.5 (Fixed)	—	0.1	17.5
$u_{69}$	H(11)...H(16)	248.1(8)	17.5 (Fixed)	—	0.1	17.5
$u_{70}$	H(10)...H(15)	248.8(7)	17.6 (Fixed)	—	0.1	17.6
$u_{71}$	H(8)...H(14)	248.8(7)	17.6 (Fixed)	—	0.1	17.6
$u_{72}$	C(2)...N(12)	249.3(3)	7.8(6)	7.0(7)	-0.2	7.0
$u_{73}$	C(3)...N(12)	249.3(3)	7.8 (Tied to $u_{72}$ )	—	-0.2	7.0
$u_{74}$	C(2)...C(3)	246.2(8)	7.8(8)	7.2(7)	-0.2	7.2
$u_{75}$	C(1)...C(9)	251.2(5)	7.6(7)	7.1(7)	-0.2	7.1
$u_{76}$	C(1)...C(6)	251.2(5)	7.6 (Tied to $u_{75}$ )	—	-0.2	7.1
$u_{77}$	H(8)...H(13)	251.2(7)	16.3 (Fixed)	—	0.2	16.3
$u_{78}$	H(10)...H(16)	251.2(7)	16.3 (Fixed)	—	0.2	16.3
$u_{79}$	H(15)...H(19)	252.7(9)	27.7 (Fixed)	—	2.5	27.7
$u_{80}$	H(14)...H(19)	252.7(9)	27.7 (Fixed)	—	2.5	27.7
$u_{81}$	H(5)...H(8)	250.4(8)	16.4 (Fixed)	—	0.2	16.4
$u_{82}$	H(5)...H(10)	250.4(8)	16.4 (Fixed)	—	0.2	16.4
$u_{83}$	H(7)...H(21)	254.6(8)	24.6 (Fixed)	—	0.7	24.6
$u_{84}$	H(11)...H(21)	254.6(8)	24.6 (Fixed)	—	0.7	24.6
$u_{85}$	C(9)...B(17)	259.8(5)	8.7(8)	8.6(9)	0.1	8.6



$u_{86}$	C(6)...B(17)	259.8(5)	8.7 (Tied to $u_{85}$ )	—	0.1	8.6
$u_{87}$	H(4)...H(14)	262.3(11)	25.4 (Fixed)	—	0.7	25.4
$u_{88}$	H(4)...H(15)	262.3(11)	25.4 (Fixed)	—	0.7	25.4
$u_{89}$	H(7)...H(11)	259.3(17)	25.4 (Fixed)	—	0.7	25.4
$u_{90}$	C(9)...H(14)	266.0(8)	15.7(19)	15.7(16)	-0.3	15.7
$u_{91}$	C(6)...H(15)	266.0(8)	15.7 (Tied to $u_{90}$ )	—	-0.3	15.7
$u_{92}$	C(3)...H(21)	268.0(6)	17.9(14)	15.8(16)	-0.3	15.8
$u_{93}$	C(2)...H(21)	268.0(6)	17.9 (Tied to $u_{92}$ )	—	-0.3	15.8
$u_{94}$	H(16)...B(17)	272.3(7)	17.5 (Tied to $u_{92}$ )	—	0.4	15.5
$u_{95}$	H(13)...B(17)	272.3(7)	17.5 (Tied to $u_{92}$ )	—	0.4	15.5
$u_{96}$	H(14)...B(17)	275.2(7)	19.1 (Tied to $u_{92}$ )	—	0.0	16.9
$u_{97}$	H(15)...B(17)	275.2(7)	19.1 (Tied to $u_{92}$ )	—	0.0	16.9
$u_{98}$	H(11)...N(12)	277.3(6)	18.8 (Fixed)	16.2(16)	-0.4	16.2
$u_{99}$	H(7)...N(12)	277.3(6)	18.8 (Tied to $u_{98}$ )	—	-0.4	16.2
$u_{100}$	C(2)...H(11)	274.8(11)	19.0 (Tied to $u_{98}$ )	—	-0.3	16.4
$u_{101}$	C(3)...H(7)	274.8(11)	19.0 (Tied to $u_{98}$ )	—	-0.3	16.4
$u_{102}$	H(4)...C(6)	278.8(7)	18.4 (Tied to $u_{92}$ )	—	-0.3	16.3
$u_{103}$	H(4)...C(9)	278.8(7)	18.4 (Tied to $u_{92}$ )	—	-0.3	16.3
$u_{104}$	C(1)...H(15)	278.3(9)	18.6 (Tied to $u_{92}$ )	—	-0.3	16.5
$u_{105}$	C(1)...H(14)	278.3(9)	18.6 (Tied to $u_{92}$ )	—	-0.3	16.5
$u_{106}$	C(9)...H(20)	280.4(7)	21.0 (Tied to $u_{98}$ )	—	0.4	18.1
$u_{107}$	C(6)...H(18)	280.4(7)	21.0 (Tied to $u_{98}$ )	—	0.4	18.1

$u_{108}$	C(6)...H(19)	284.1(7)	23.4 (Tied to $u_{98}$ )	—	0.0	20.1
$u_{109}$	C(9)...H(19)	284.1(7)	23.4 (Tied to $u_{98}$ )	—	0.0	20.1
$u_{110}$	C(2)...C(9)	288.0(4)	8.0(3)	7.5(8)	-0.4	7.5
$u_{111}$	C(3)...C(6)	288.0(4)	8.0 (Tied to $u_{110}$ )	—	-0.4	7.5
$u_{112}$	H(14)...H(21)	289.8(6)	12.2 (Fixed)	—	-1.3	12.2
$u_{113}$	H(15)...H(21)	289.8(6)	12.2 (Fixed)	—	-1.3	12.2
$u_{114}$	C(1)...N(12)	295.2(5)	9.4(6)	7.5(8)	-0.4	7.5
$u_{115}$	H(4)...H(11)	305.0(10)	12.6 (Fixed)	—	-1.2	12.6
$u_{116}$	H(4)...H(7)	305.0(10)	12.6 (Fixed)	—	-1.2	12.6
$u_{117}$	H(7)...H(14)	305.6(5)	12.5 (Fixed)	—	-1.2	12.5
$u_{118}$	H(11)...H(15)	305.6(5)	12.5 (Fixed)	—	-1.2	12.5
$u_{119}$	H(19)...H(21)	308.3(8)	13.5 (Fixed)	—	-1.9	13.5
$u_{120}$	H(14)...H(18)	309.5(8)	27.6 (Fixed)	—	-0.8	27.6
$u_{121}$	H(15)...H(20)	309.5(8)	27.6 (Fixed)	—	-0.8	27.6
$u_{122}$	H(16)...H(19)	309.3(8)	28.5 (Fixed)	—	-0.8	28.5
$u_{123}$	H(13)...H(19)	309.3(8)	28.5 (Fixed)	—	-0.8	28.5
$u_{124}$	C(1)...H(21)	326.1(8)	17.3(16)	16.2(16)	-0.8	16.2
$u_{125}$	C(2)...H(15)	326.5(6)	15.5(20)	16.4(16)	-0.8	16.4
$u_{126}$	C(3)...H(14)	326.5(6)	15.5 (Tied to $u_{125}$ )	—	-0.8	16.4
$u_{127}$	C(6)...H(11)	329.8(6)	17.3 (Tied to $u_{124}$ )	—	-0.8	16.2
$u_{128}$	H(7)...C(9)	329.8(6)	17.3 (Tied to $u_{124}$ )	—	-0.8	16.2
$u_{129}$	H(4)...N(12)	335.5(8)	16.3(20)	16.2(16)	-0.8	16.2

$u_{130}$	C(6)...H(16)	335.2(4)	10.8 (Tied to $u_{124}$ )	—	-1.0	10.2
$u_{131}$	C(9)...H(13)	335.2(4)	10.8 (Tied to $u_{124}$ )	—	-1.0	10.2
$u_{132}$	H(10)...N(12)	341.5(4)	11.3(12)	10.2(10)	-1.1	10.2
$u_{133}$	H(8)...N(12)	341.5(4)	11.3 (Tied to $u_{132}$ )	—	-1.1	10.2
$u_{134}$	C(3)...H(8)	341.2(9)	11.6(6)	10.2(10)	-1.0	10.2
$u_{135}$	C(2)...H(10)	341.2(9)	11.6 (Tied to $u_{134}$ )	—	-1.0	10.2
$u_{136}$	H(5)...C(9)	345.6(6)	11.6 (Tied to $u_{134}$ )	—	-1.0	10.2
$u_{137}$	H(5)...C(6)	345.6(6)	11.6 (Tied to $u_{134}$ )	—	-1.0	10.2
$u_{138}$	C(1)...H(16)	346.9(6)	11.5 (Tied to $u_{134}$ )	—	-1.0	10.2
$u_{139}$	C(1)...H(13)	346.9(6)	11.5 (Tied to $u_{134}$ )	—	-1.0	10.2
$u_{140}$	C(6)...H(20)	356.7(6)	9.1(11)	11.5(11)	-1.8	11.5
$u_{141}$	C(9)...H(18)	356.7(6)	9.1 (Tied to $u_{140}$ )	—	-1.8	11.5
$u_{142}$	H(13)...H(15)	362.1(8)	17.3 (Fixed)	—	-1.4	17.3
$u_{143}$	H(14)...H(16)	362.1(8)	17.3 (Fixed)	—	-1.4	17.3
$u_{144}$	H(8)...H(21)	366.2(6)	17.2 (Fixed)	—	-1.4	17.2
$u_{145}$	H(10)...H(21)	366.2(6)	17.2 (Fixed)	—	-1.4	17.2
$u_{146}$	H(16)...H(18)	377.0(7)	17.5 (Fixed)	—	-2.0	17.5
$u_{147}$	H(13)...H(20)	377.0(7)	17.5 (Fixed)	—	-2.0	17.5
$u_{148}$	H(8)...H(11)	375.1(12)	17.8 (Fixed)	—	-1.4	17.8
$u_{149}$	H(7)...H(10)	375.1(12)	17.8 (Fixed)	—	-1.4	17.8
$u_{150}$	H(4)...H(13)	379.1(8)	17.9 (Fixed)	—	-1.3	17.9
$u_{151}$	H(4)...H(16)	379.1(8)	17.9 (Fixed)	—	-1.3	17.9

$u_{152}$	H(5)...H(15)	378.9(10)	17.9 (Fixed)	—	-1.4	17.9
$u_{153}$	H(5)...H(14)	378.9(10)	17.9 (Fixed)	—	-1.4	17.9
$u_{154}$	H(14)...H(20)	380.5(7)	18.5 (Fixed)	—	-2.5	18.5
$u_{155}$	H(15)...H(18)	380.5(7)	18.5 (Fixed)	—	-2.5	18.5
$u_{156}$	C(6)...H(10)	385.5(5)	13.9(10)	11.1(10)	-1.4	11.1
$u_{157}$	H(8)...C(9)	385.5(5)	13.9 (Tied to $u_{156}$ )	—	-1.4	11.1
$u_{158}$	C(2)...H(16)	386.2(5)	13.6 (Tied to $u_{156}$ )	—	-1.4	10.9
$u_{159}$	C(3)...H(13)	386.2(5)	13.6 (Tied to $u_{156}$ )	—	-1.4	10.9
$u_{160}$	H(5)...N(12)	393.3(6)	11.1 (Fixed)	—	-1.4	11.1
$u_{161}$	H(4)...H(21)	392.3(9)	17.8 (Fixed)	—	-1.8	17.8
$u_{162}$	C(2)...B(17)	396.1(6)	12.3(4)	8.6(9)	-0.8	8.6
$u_{163}$	C(3)...B(17)	396.1(6)	12.3 (Tied to $u_{162}$ )	—	-0.8	8.6
$u_{164}$	H(7)...H(15)	395.0(7)	17.9 (Fixed)	—	-1.9	17.9
$u_{165}$	H(11)...H(14)	395.0(7)	17.9 (Fixed)	—	-1.9	17.9
$u_{166}$	H(5)...H(21)	407.5(9)	21.2 (Fixed)	—	-1.5	21.2
$u_{167}$	H(8)...H(15)	405.5(8)	21.6 (Fixed)	—	-1.6	21.6
$u_{168}$	H(10)...H(14)	405.5(8)	21.6 (Fixed)	—	-1.6	21.6
$u_{169}$	H(11)...H(13)	410.5(8)	21.3 (Fixed)	—	-1.6	21.3
$u_{170}$	H(7)...H(16)	410.5(8)	21.3 (Fixed)	—	-1.6	21.3
$u_{171}$	H(13)...H(16)	413.7(7)	13.7 (Fixed)	—	-1.8	13.7
$u_{172}$	C(2)...H(18)	421.1(8)	15.1(12)	17.6(10)	-0.8	17.6
$u_{173}$	C(3)...H(20)	421.1(8)	15.1 (Tied to $u_{172}$ )	—	-0.8	17.6

$u_{174}$	C(3)...H(19)	425.8(8)	17.7(12)	18.8(10)	-1.4	18.8
$u_{175}$	C(2)...H(19)	425.8(8)	17.7 (Tied to $u_{174}$ )	—	-1.4	18.8
$u_{176}$	H(11)...B(17)	427.4(8)	14.3(20)	17.5(18)	-1.1	17.5
$u_{177}$	H(7)...B(17)	427.4(8)	14.3 (Tied to $u_{176}$ )	—	-1.1	17.5
$u_{178}$	H(8)...H(10)	424.9(11)	13.8 (Fixed)	—	-1.8	13.8
$u_{179}$	H(5)...H(13)	430.5(7)	13.8 (Fixed)	—	-1.8	13.8
$u_{180}$	H(5)...H(16)	430.5(7)	13.8 (Fixed)	—	-1.8	13.8
$u_{181}$	H(7)...H(18)	437.5(10)	24.6 (Fixed)	—	-0.4	24.6
$u_{182}$	H(11)...H(20)	437.5(10)	24.6 (Fixed)	—	-0.4	24.6
$u_{183}$	C(1)...B(17)	448.4(7)	12.6(8)	9.5(10)	-1.2	9.5
$u_{184}$	H(4)...H(19)	453.6(13)	31.7 (Fixed)	—	-0.2	31.7
$u_{185}$	C(1)...H(19)	462.5(10)	20.3(25)	20.4(20)	-1.3	20.4
$u_{186}$	H(4)...B(17)	467.8(10)	19.5(21)	21.3(20)	-1.4	21.3
$u_{187}$	H(8)...B(17)	472.4(6)	12.0 (Fixed)	—	-1.6	13.1
$u_{188}$	H(10)...B(17)	472.4(6)	12.0 (Tied to $u_{186}$ )	—	-1.6	13.1
$u_{189}$	C(2)...H(20)	475.2(7)	13.2(14)	13.3(13)	-2.4	13.3
$u_{190}$	C(3)...H(18)	475.2(7)	13.2 (Tied to $u_{189}$ )	—	-2.4	13.3
$u_{191}$	H(8)...H(18)	483.1(8)	21.9 (Fixed)	—	-1.2	21.9
$u_{192}$	H(10)...H(20)	483.1(8)	21.9 (Fixed)	—	-1.2	21.9
$u_{193}$	H(11)...H(19)	481.8(8)	20.4 (Fixed)	—	-2.9	20.4
$u_{194}$	H(7)...H(19)	481.8(8)	20.4 (Fixed)	—	-2.9	20.4
$u_{195}$	H(8)...H(19)	487.5(9)	25.1 (Fixed)	—	-1.8	25.1

$u_{196}$	H(10)...H(19)	487.5(9)	25.1 (Fixed)	—	-1.8	25.1
$u_{197}$	H(10)...H(13)	488.1(6)	12.8 (Fixed)	—	-2.7	12.8
$u_{198}$	H(8)...H(16)	488.1(6)	12.8 (Fixed)	—	-2.7	12.8
$u_{199}$	H(7)...H(20)	492.6(9)	23.4 (Fixed)	—	-2.3	23.4
$u_{200}$	H(11)...H(18)	492.6(9)	23.4 (Fixed)	—	-2.3	23.4
$u_{201}$	C(1)...H(18)	506.8(8)	13.9(14)	15.4(15)	-2.3	15.4
$u_{202}$	C(1)...H(20)	506.8(8)	13.9 (Tied to $u_{201}$ )	—	-2.3	15.4
$u_{203}$	H(4)...H(20)	533.6(10)	24.2 (Fixed)	—	-3.1	24.2
$u_{204}$	H(4)...H(18)	533.6(10)	24.2 (Fixed)	—	-3.1	24.2
$u_{205}$	H(5)...B(17)	551.0(7)	11.6 (Fixed)	—	-2.5	11.6
$u_{206}$	H(10)...H(18)	563.2(7)	15.0 (Fixed)	—	-4.0	15.0
$u_{207}$	H(8)...H(20)	563.2(7)	15.0 (Fixed)	—	-4.0	15.0
$u_{208}$	H(5)...H(19)	570.0(10)	21.2 (Fixed)	—	-3.0	21.2
$u_{209}$	H(5)...H(18)	604.0(9)	17.7 (Fixed)	—	-3.6	17.7
$u_{210}$	H(5)...H(20)	604.0(9)	17.7 (Fixed)	—	-3.6	17.7

---

<sup>a</sup> All values are tabulated in pm.

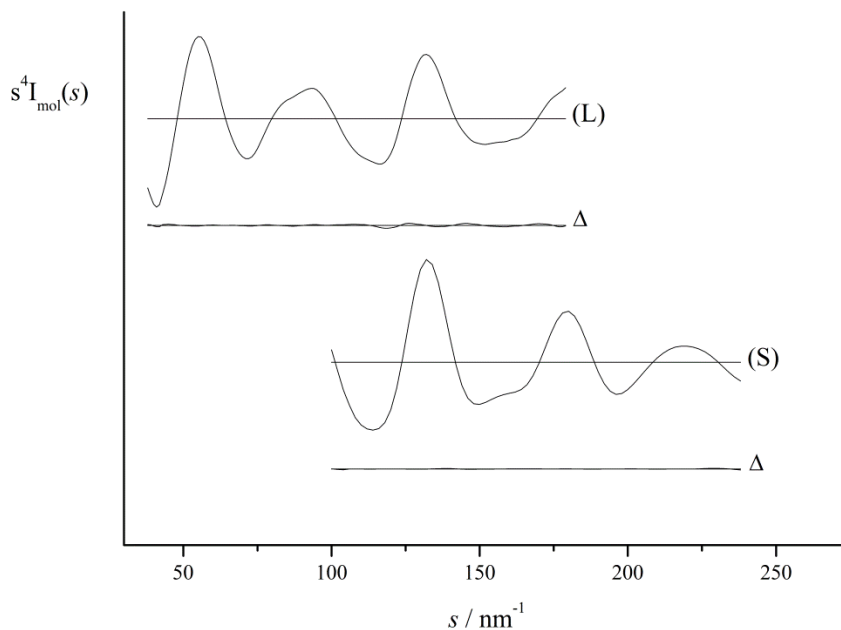


Figure S9: Experimental and final weighted difference (experimental – theoretical) MICs for **PIB** using the MP2 starting structure, vibrational corrections and restraints. L indicates data from the long nozzle-to-camera distance, S indicates data from the short nozzle-to-camera distance.

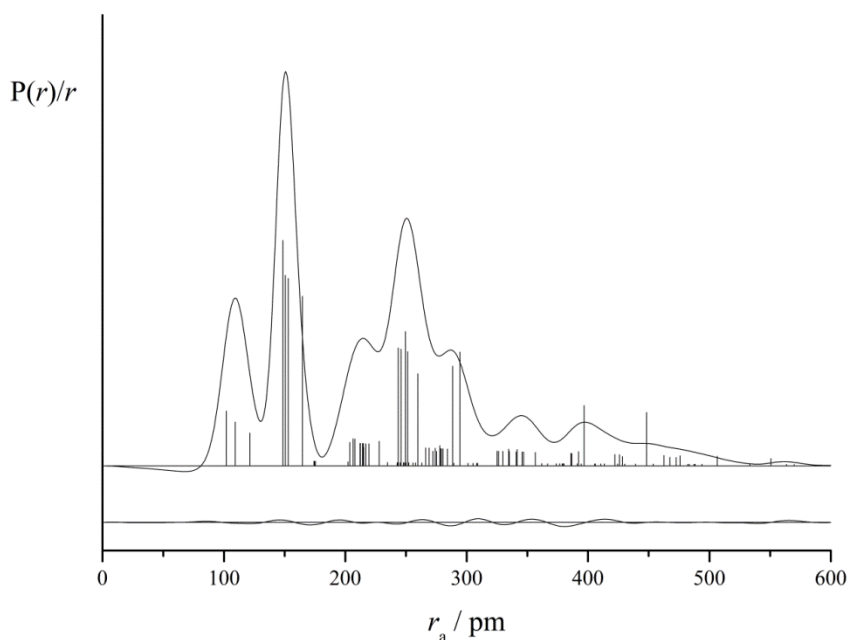


Figure 10: Experimental and difference (experimental minus theoretical) RDCs for the GED refinement of **PIB** using the MP2 starting structure, vibrational corrections and restraints. Before Fourier inversion, the data were multiplied by  $s \cdot \exp(-0.00002s^2)/(Z_C - f_C)(Z_N - f_N)$ .