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Supplementary Material

Utilising the Combined Power of Theory and Experiment to Understand Molecular Structure – Solid-State and Gas-Phase Investigation of Morpholine Borane

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Data Collection

The sample and the nozzle were at temperatures of 373 K and 378 K, respectively, during data acquisition at both the long and the short nozzle-to-image-plate distances. 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 ±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. The authors consequently expect that the vapour composition was 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. 1×10^{-6} Torr; with the sample admission valve open ca. 5%, a pressure of ca. 1×10^{-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.

Dataset	Short	Long
Nozzle-to-plate distance / mm	235.5	477.5
$T_{nozzle,\ av}$ / K	378	378
$T_{sample,\ av}$ / K	373	373
Electron wavelength / pm	5.85	5.85
Exposure Time / s	240.0	120.0
Δs / nm^{-1}	2.0	1.0
s_{min} / nm^{-1}	104.0	42.0
sw_1 / nm^{-1}	124.0	62.0
sw_2 / nm^{-1}	206.0	108.0
s_{max} / nm^{-1}	240.0	126.0
Correlation parameter	0.4654	0.4984
Scale factor (k)[A]	0.0188(6)	0.0048(2)

[A] Values in parentheses are the estimated standard deviations.

Table S2: Least-squares correlation matrix[A] (×100) for the refinement.

	p_{13}	p_{14}	u_{76}	u_{88}	k_1
p_6				-50	

p_9	59			
p_{11}		-61		
u_4				52
u_{54}			58	

[A] Only values ≥ 50% are included in the least-squares correlation matrix. k_1 is a scale factor

Table S3: Single crystal X-ray diffraction data collection, solution and refinement information.

Identification code	AJA-2MoA	AJA-2Mo-RTa
Empirical formula	$C_4H_{12}BNO$	$C_4H_{12}BNO$
Formula weight	100.96	100.96
Temperature/K	120.0(1)	297.9(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	6.8632(2)	6.9662(5)
b/Å	11.5032(3)	11.5199(8)
c/Å	8.1150(3)	8.2344(6)
α/°	90	90
β/°	105.219(3)	105.678(8)
γ/°	90	90
Volume/Å^3	618.20(3)	636.22(8)
Z	4	4
ρ_{calc}g/cm^3	1.085	1.054
μ/mm^{-1}	0.073	0.071
F(000)	224.0	224.0
Crystal size/mm^3	0.32 × 0.281 × 0.141	0.637 × 0.602 × 0.437
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.938 to 83.236	7.03 to 57.972

Index ranges	$-12 \leq h \leq 12$, $-21 \leq k \leq 21$, $-15 \leq l \leq 15$	$-9 \leq h \leq 9$, $-15 \leq k \leq 15$, $-11 \leq l \leq 10$
Reflections collected	34462	13775
Independent reflections	4226 [R_{int} = 0.0519, R_{sigma} = 0.0335]	1693 [R_{int} = 0.1578, R_{sigma} = 0.0666]
Data/restraints/parameters	4226/0/100	1693/0/100
Goodness-of-fit on F^2	1.065	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0481, wR_2 = 0.1267	R_1 = 0.0758, wR_2 = 0.2107
Final R indexes [all data]	R_1 = 0.0806, wR_2 = 0.1510	R_1 = 0.0888, wR_2 = 0.2292
Largest diff. peak/hole / e $Å^{-3}$	0.34/-0.23	0.26/-0.33

Table S4: Calculated coordinates at the MP2(full)/6-31G* level for **MBC**.

Atom	*x*	*y*	*z*
N	0.53114	0.87930	0.00000
C	-0.10307	0.30921	1.21464
C	-0.10307	0.30921	-1.21464
B	0.52185	2.51869	0.00000
C	-0.10307	-1.20668	-1.16653
H	-1.12451	0.69564	-1.23862
H	0.43395	0.69573	-2.08445
C	-0.10307	-1.20668	1.16653
H	-1.12451	0.69564	1.23862
H	0.43395	0.69573	2.08445
O	-0.76598	-1.67949	0.00000
H	0.93042	-1.59127	-1.19544
H	-0.64521	-1.61952	-2.02049
H	0.93042	-1.59127	1.19544
H	-0.64521	-1.61952	2.02049
H	-0.64937	2.82938	0.00000
H	1.10781	2.83206	-1.01344

H	1.10781	2.83206	1.01344
H	1.51881	0.60230	0.00000

Table S5: Calculated coordinates at the MP2(full)/6-311G* level for **MBC**.

Atom	*x*	*y*	*z*
N	0.53185	0.88599	0.00000
C	-0.10068	0.30868	1.21093
C	-0.10068	0.30868	-1.21093
B	0.50833	2.51653	0.00000
C	-0.10068	-1.20847	-1.15845
H	-1.12244	0.69255	-1.23712
H	0.43387	0.69027	-2.08343
C	-0.10068	-1.20847	1.15845
H	-1.12244	0.69255	1.23712
H	0.43387	0.69027	2.08343
O	-0.76187	-1.68354	0.00000
H	0.93244	-1.59276	-1.18520
H	-0.63813	-1.61753	-2.01580
H	0.93244	-1.59276	1.18520
H	-0.63813	-1.61753	2.01580
H	-0.66446	2.82791	0.00000
H	1.09147	2.84430	-1.01324
H	1.09147	2.84430	1.01324
H	1.51664	0.61961	0.00000

Table S6: Calculated coordinates at the MP2(full)/6-311+G* level for **MBC**.

Atom	*x*	*y*	*z*
N	0.53341	0.88375	0.00000
C	-0.10512	0.31039	1.20889
C	-0.10512	0.31039	-1.20889
B	0.52469	2.51564	0.00000
C	-0.10512	-1.20643	-1.16149
H	-1.12636	0.69766	-1.23240
H	0.42613	0.69196	-2.08385
C	-0.10512	-1.20643	1.16149
H	-1.12636	0.69766	1.23240
H	0.42613	0.69196	2.08385
O	-0.76121	-1.68728	0.00000
H	0.92729	-1.59264	-1.19033
H	-0.64503	-1.61546	-2.01742
H	0.92729	-1.59264	1.19033
H	-0.64503	-1.61546	2.01742
H	-0.64756	2.83419	0.00000
H	1.11040	2.83927	-1.01410
H	1.11040	2.83927	1.01410
H	1.51803	0.61045	0.00000

Table S7: Calculated coordinates at the CBS-QB3 level for **MBC**.

Atom	*x*	*y*	*z*
N	0.41148	0.60493	-0.00000
C	-0.21682	0.02303	1.22279
C	-0.21682	0.02303	-1.22279
B	0.40865	2.24904	-0.00000
C	-0.21682	-1.50052	-1.17274
H	-1.23601	0.41080	-1.26208
H	0.32664	0.40168	-2.08949
C	-0.21682	-1.50052	1.17274
H	-1.23601	0.41080	1.26208
H	0.32664	0.40168	2.08949
O	-0.85758	-1.98251	-0.00000
H	0.81585	-1.88462	-1.22144
H	-0.76867	-1.90674	-2.02161
H	0.81585	-1.88462	1.22144
H	-0.76867	-1.90674	2.02161
H	-0.75631	2.57531	-0.00000
H	0.99524	2.56654	-1.01035
H	0.99524	2.56654	1.01035
H	1.39496	0.33288	-0.00000

Table S8: Calculated coordinates at the CBS-QB3 level for **MBC**$_{TS1}$

Atom	*x*	*y*	*z*
C	0.12972	-1.21272	-0.62713
C	0.12972	1.21272	-0.62713
H	-0.48058	-2.09252	-0.41288
H	0.45619	-1.26933	-1.67356
H	0.45619	1.26933	-1.67356
H	-0.48058	2.09252	-0.41288
N	-0.67377	-0.00000	-0.43215
H	-2.06901	-0.00000	-0.66384
B	-1.78085	-0.00000	0.69365
H	-2.88914	-0.00000	-0.14076
H	-1.90549	1.02866	1.28625
H	-1.90549	-1.02866	1.28625
C	1.36251	-1.17932	0.27606
H	2.02621	-2.02156	0.06876
H	1.05356	-1.22699	1.33162
C	1.36251	1.17932	0.27606
H	1.05356	1.22699	1.33162
H	2.02621	2.02156	0.06876
O	2.12848	-0.00000	0.04485

Table S9: Calculated coordinates at the CBS-QB3 level for **MBC---BH_3**

Atom	*x*	*y*	*z*
C	2.26587	-0.82556	-0.50727
O	2.70041	0.37857	0.10576
C	1.72104	1.40190	-0.01734
C	0.40699	0.99528	0.63724
C	0.97587	-1.33890	0.12204
H	2.12637	2.28627	0.47538
H	2.12495	-0.67049	-1.58916
H	3.06447	-1.55579	-0.37063
H	0.54158	0.83121	1.70741
H	-0.36774	1.74742	0.48813
H	1.12851	-1.57889	1.17578
H	0.60506	-2.22925	-0.38726
H	1.56012	1.64475	-1.07962
N	-0.09523	-0.29548	0.06288
H	-0.32844	-0.12365	-0.91944
B	-1.47149	-0.80238	0.71047
H	-1.78242	-1.84377	0.21874
H	-1.36748	-0.78866	1.90750
H	-2.33804	0.11531	0.54437
B	-2.79374	0.57703	-0.66407
H	-2.58700	1.74196	-0.43464
H	-3.93235	0.21640	-0.60722
H	-2.15732	0.11674	-1.57906

Table S10: Calculated coordinates at the CBS-QB3 level for **MBC**$_{TS2}$

Atom	*x*	*y*	*z*
C	1.91757	0.94709	0.64092
O	2.60247	-0.19123	0.13733
C	1.71618	-1.29494	-0.00411
C	0.58035	-0.97318	-0.96951
C	0.78740	1.37425	-0.29195
H	2.31211	-2.12668	-0.38280
H	1.52151	0.73140	1.64560
H	2.65765	1.74411	0.72851
H	0.99349	-0.82105	-1.97445
H	-0.13084	-1.79960	-1.01286
H	1.21472	1.71697	-1.24242
H	0.22474	2.20326	0.14312
H	1.31083	-1.57833	0.97923
N	-0.14326	0.24813	-0.54159
H	-0.85452	-0.03508	0.77165
B	-1.43950	0.54659	-1.17743
H	-1.77984	1.68621	-1.21306
H	-1.91658	-0.26708	-1.89842
H	-2.59322	0.27254	0.13615
B	-2.39586	-0.47953	1.09587
H	-2.26292	-1.62872	0.79428
H	-3.08897	-0.22691	2.03912
H	-1.23351	-0.04821	1.59683

Table S11: Calculated coordinates at the CBS-QB3 level for **MBC–P**

Atom	*x*	*y*	*z*
N	0.27531	0.87652	0.00000
C	-0.34860	0.33832	1.21353
C	-0.34860	0.33832	-1.21353
B	1.34439	1.76380	0.00000
C	-0.34860	-1.19014	-1.17487
H	-1.38653	0.69023	-1.27779
H	0.19620	0.70332	-2.08517
C	-0.34860	-1.19014	1.17487
H	-1.38653	0.69023	1.27779
H	0.19620	0.70332	2.08517
O	-0.98934	-1.67292	0.00000
H	0.68713	-1.56040	-1.21975
H	-0.90441	-1.59943	-2.02061
H	0.68713	-1.56040	1.21975
H	-0.90441	-1.59943	2.02061
H	1.78964	2.13440	-1.04318
H	1.78964	2.13440	1.04318

Table S12: 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. All energies are in Hartrees.

Molecule	E_{CBS}	*H*	*G*	*ZPE*
MBC	-314.07056293	0.178873	0.140412	0.170926
MBC-P	-312.89166544	0.156247	0.118902	0.148879
MP	-287.45874284	0.142679	0.107995	0.13643
BH_3	-26.53758955	0.030634	0.026981	0.009274
H_2	-1.17447357	0.013451793	-0.001421	0.010146614

Table S13: 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. All energies are in Hartrees.

Molecule	$E_{CBS\text{-}QB3}$	*H*	*G*	*ZPE*
MBC	-313.8662327	0.176547	0.137891	0.168484
MBC-P	-312.702707	0.154171	0.116685	0.146735
MP	-287.282459	0.140714	0.105846	0.134377
BH_3	-26.50827404	0.029974	0.008598	0.026144
H_2	-1.16275987	0.013374	-0.001327	0.010069

Table S14. Internuclear distances (r_a / pm), refined (u_{GED}) and theoretical (u_{h1}) amplitudes of vibration and restraints and distance corrections (k_{h1})[A].

Amp.	Atomic Pair	r_a	u_{GED}	Restraint	k_{h1}	u_{h1}
u_1	N(1)-H(19)	102.2(7)	7.0(8)	7.2(7)	0.4	7.2
u_4	C(2)-H(10)	109.5(1)	6.2 (Tied to u2)	–	0.4	7.6
u_5	C(3)-H(7)	109.5(1)	6.2 (Tied to u2)	–	0.4	7.6
u_2	C(8)-H(15)	109.5(1)	6.2(4)	7.6(8)	0.4	7.6
u_3	C(5)-H(13)	109.5(1)	6.2 (Tied to u2)	–	0.4	7.6
u_6	C(2)-H(9)	109.5(1)	6.2 (Tied to u2)	–	0.4	7.6
u_7	C(3)-H(6)	109.5(1)	6.2 (Tied to u2)	–	0.4	7.6
u_8	C(5)-H(12)	109.5(1)	6.4 (Tied to u2)	–	0.4	7.8
u_9	C(8)-H(14)	109.5(1)	6.4 (Tied to u2)	–	0.4	7.8
u_{11}	B(4)-H(17)	121.3(4)	8.9 (Tied to u10)	–	0.5	8.6
u_{12}	B(4)-H(18)	121.3(4)	8.9 (Tied to u10)	–	0.5	8.6
u_{10}	B(4)-H(16)	121.3(4)	8.9(10)	8.6(9)	0.5	8.6
u_{13}	C(8)-O(11)	142.5(5)	4.8(5)	4.8(5)	0.1	4.8
u_{14}	C(5)-O(11)	142.5(5)	4.8 (Tied to u13)	–	0.1	4.8
u_{15}	N(1)-C(3)	148.2(2)	5.2(6)	5.0(5)	0.2	5.0
u_{16}	N(1)-C(2)	148.2(2)	5.2 (Tied to u15)	–	0.2	5.0
u_{17}	C(3)-C(5)	152.2(6)	5.3(10)	–	0.1	5.1

u_{18}	C(2)-C(8)	152.2(6)	5.3 (Tied to u17)	–	0.1	5.1
u_{19}	N(1)-B(4)	164.2(7)	5.6(7)	6.2(6)	0.3	6.2
u_{22}	H(12)...H(13)	176.9(6)	12.2 (fixed)	–	0.1	12.2
u_{23}	H(14)...H(15)	176.9(6)	12.2 (fixed)	–	0.1	12.2
u_{20}	H(6)...H(7)	177.2(6)	12.3 (fixed)	–	0.1	12.3
u_{21}	H(9)...H(10)	177.2(6)	12.3 (fixed)	–	0.1	12.3
u_{24}	O(11)...H(15)	200.0(8)	9.7(10)	10.2(10)	-0.1	10.2
u_{25}	O(11)...H(13)	200.0(8)	9.7 (Tied to u24)	–	-0.1	10.2
u_{26}	H(17)...H(18)	202.1(7)	13.7 (fixed)	–	0.1	13.7
u_{27}	H(16)...H(18)	202.1(7)	13.7 (fixed)	–	0.1	13.7
u_{28}	H(16)...H(17)	202.1(7)	13.7 (fixed)	–	0.1	13.7
u_{30}	C(2)...H(19)	203.8(7)	10.3 (fixed)	–	-0.1	10.3
u_{29}	C(3)...H(19)	203.8(7)	10.3 (fixed)	–	-0.1	10.3
u_{33}	N(1)...H(6)	206.6(5)	10.9 (Tied to u31)	–	-0.1	10.3
u_{34}	N(1)...H(9)	206.6(5)	10.9 (Tied to u31)	–	-0.1	10.3
u_{35}	N(1)...H(10)	208.7(5)	11.0 (Tied to u31)	–	-0.1	10.4
u_{36}	N(1)...H(7)	208.7(5)	11.0 (Tied to u31)	–	-0.1	10.4
u_{32}	O(11)...H(12)	209.5(15)	10.6 (Tied to u31)	–	-0.1	10.0
u_{31}	O(11)...H(14)	209.5(15)	10.6(7)	10.0(10)	-0.1	10.0
u_{37}	B(4)...H(19)	214.7(9)	11.8 (fixed)	–	-0.1	11.8
u_{43}	C(2)...H(14)	215.2(7)	10.6 (fixed)	–	-0.1	10.6
u_{42}	C(3)...H(12)	215.2(7)	10.6 (fixed)	–	-0.1	10.6
u_{38}	C(3)...H(13)	215.3(7)	10.7 (fixed)	–	-0.1	10.7
u_{39}	C(2)...H(15)	215.3(7)	10.7 (fixed)	–	-0.1	10.7
u_{45}	C(8)...H(10)	216.2(8)	10.7 (fixed)	–	-0.1	10.7
u_{44}	C(5)...H(7)	216.2(8)	10.7 (fixed)	–	-0.1	10.7
u_{40}	C(5)...H(6)	217.5(9)	10.8 (fixed)	–	-0.1	10.8

u_{41}	C(8)...H(9)	217.5(9)	10.8 (fixed)	–	-0.1	10.8
u_{46}	N(1)...H(17)	227.7(8)	11.9 (fixed)	–	-0.2	11.9
u_{47}	N(1)...H(18)	227.7(8)	11.9 (fixed)	–	-0.2	11.9
u_{48}	N(1)...H(16)	227.7(8)	11.8 (fixed)	–	-0.2	11.8
u_{49}	C(5)...C(8)	228.7(12)	6.2(7)	6.6(7)	-0.2	6.6
u_{51}	H(10)...H(19)	233.5(9)	16.5(fixed)	–	0.0	16.5
u_{50}	H(7)...H(19)	233.5(9)	16.5(fixed)	–	0.0	16.5
u_{52}	H(12)...H(14)	235.1(27)	23.0(fixed)	–	0.8	23.0
u_{53}	C(2)...C(3)	239.4(7)	7.4(7)	6.9(7)	-0.2	6.9
u_{56}	H(6)...H(9)	242.5(6)	23.3(5)	–	0.7	23.3
u_{54}	C(3)...O(11)	242.5(6)	6.6 (Tied to u54)	–	-0.2	6.6
u_{55}	C(2)...O(11)	242.7(22)	6.6 (fixed)	–	-0.2	6.6
u_{66}	H(10)...H(14)	246.4(11)	17.5 (fixed)	–	-0.0	17.5
u_{65}	H(7)...H(12)	246.4(11)	17.5 (fixed)	–	-0.0	17.5
u_{59}	H(17)...H(19)	247.2(11)	20.2 (fixed)	–	0.2	20.2
u_{60}	H(18)...H(19)	247.2(11)	20.2 (fixed)	–	0.2	20.2
u_{57}	N(1)...C(5)	247.6(6)	6.7 (Tied to u54)	–	-0.2	6.7
u_{58}	N(1)...C(8)	247.6(6)	6.7 (Tied to u54)	–	-0.2	6.7
u_{62}	H(6)...H(13)	249.5(9)	17.3 (fixed)	–	0.0	17.3
u_{61}	H(9)...H(15)	249.5(9)	17.3 (fixed)	–	0.0	17.3
u_{70}	H(7)...H(13)	252.9(7)	16.1 (fixed)	–	0.2	16.1
u_{69}	H(10)...H(15)	252.9(7)	16.1 (fixed)	–	0.2	16.1
u_{68}	H(6)...H(16)	253.0(14)	26.8 (fixed)	–	2.3	26.8
u_{67}	H(9)...H(16)	253.0(14)	26.8 (fixed)	–	2.3	26.8
u_{63}	H(7)...H(17)	253.1(12)	24.3 (fixed)	–	3.0	24.3
u_{64}	H(10)...H(18)	253.1(12)	24.3 (fixed)	–	3.0	24.3
u_{71}	H(12)...H(19)	254.1(11)	23.8 (fixed)	–	0.6	23.8

u_{72}	H(14)...H(19)	254.1(11)	23.8 (fixed)	–	0.6	23.8
u_{76}	C(5)...H(14)	256.1(16)	14.9 (fixed)	–	-0.2	14.9
u_{75}	C(8)...H(12)	256.1(16)	14.9 (fixed)	–	-0.2	14.9
u_{74}	C(3)...B(4)	261.3(6)	7.9 (Tied to u73)	–	0.1	8.5
u_{73}	C(2)...B(4)	261.3(6)	7.9(9)	8.5(9)	0.1	8.5
u_{77}	C(3)...H(9)	264.4(12)	15.3 (fixed)	–	-0.3	15.3
u_{78}	C(2)...H(6)	264.4(12)	15.3 (fixed)	–	-0.3	15.3
u_{80}	C(8)...H(19)	267.9(10)	15.2 (fixed)	–	-0.3	15.2
u_{79}	C(5)...H(19)	267.9(10)	15.2 (fixed)	–	-0.3	15.2
u_{81}	H(9)...O(11)	269.7(14)	16.1 (fixed)	–	-0.3	16.1
u_{82}	H(6)...O(11)	269.7(14)	16.1 (fixed)	–	-0.3	16.1
u_{87}	N(1)...H(14)	275.8(8)	15.7 (fixed)	–	-0.3	15.7
u_{88}	N(1)...H(12)	275.8(8)	15.7 (fixed)	–	-0.3	15.7
u_{84}	B(4)...H(9)	276.0(9)	16.5 (fixed)	–	0.1	16.5
u_{83}	B(4)...H(6)	276.0(9)	16.5 (fixed)	–	0.1	16.5
u_{92}	C(2)...C(5)	278.8(6)	9.2 (Tied to u91)	–	-0.4	7.0
u_{91}	C(3)...C(8)	278.8(6)	9.2(6)	7.0(7)	-0.4	7.0
u_{86}	B(4)...H(7)	278.8(9)	15.4 (fixed)	–	0.4	15.4
u_{85}	B(4)...H(10)	278.8(9)	15.4 (fixed)	–	0.4	15.4
u_{90}	C(3)...H(17)	283.1(8)	18.2 (fixed)	–	0.3	18.2
u_{89}	C(2)...H(18)	283.1(8)	18.2 (fixed)	–	0.3	18.2
u_{94}	C(2)...H(16)	286.0(10)	19.3 (fixed)	–	0.0	19.3
u_{93}	C(3)...H(16)	286.0(10)	19.3 (fixed)	–	0.0	19.3
u_{96}	H(9)...H(19)	289.9(7)	12.1 (fixed)	–	-1.2	12.1
u_{97}	H(6)...H(19)	289.9(7)	12.1 (fixed)	–	-1.2	12.1
u_{95}	N(1)...O(11)	290.2(4)	5.4(7)	–	-0.4	7.3
u_{98}	H(9)...H(14)	306.5(7)	12.5 (fixed)	–	-1.1	12.5

u_{99}	H(6)...H(12)	306.5(7)	12.5 (fixed)	–	-1.1	12.5
u_{100}	H(16)...H(19)	308.2(10)	13.5 (fixed)	–	-1.8	13.5
u_{101}	H(6)...H(17)	309.7(9)	27.0 (fixed)	–	-0.8	27.0
u_{102}	H(9)...H(18)	309.7(9)	27.0 (fixed)	–	-0.8	27.0
u_{103}	H(7)...H(16)	316.9(12)	26.9 (fixed)	–	-0.8	26.9
u_{104}	H(10)...H(16)	316.9(12)	26.9 (fixed)	–	-0.8	26.9
u_{107}	C(2)...H(12)	320.0(11)	15.5 (fixed)	–	-0.7	15.5
u_{108}	C(3)...H(14)	320.0(11)	15.5 (fixed)	–	-0.8	15.5
u_{105}	C(5)...H(9)	320.2(9)	15.7 (fixed)	–	-0.8	15.8
u_{106}	H(6)...C(8)	320.2(9)	15.7 (fixed)	–	-0.8	15.7
u_{111}	C(8)...H(13)	320.5(12)	9.9 (fixed)	–	-1.0	9.9
u_{110}	C(5)...H(15)	320.5(12)	9.9 (fixed)	–	-1.0	9.9
u_{109}	O(11)...H(19)	324.9(11)	15.1 (fixed)	–	-0.7	15.1
u_{112}	C(3)...H(10)	332.9(6)	10.0 (fixed)	–	-0.9	10.0
u_{113}	C(2)...H(7)	332.9(6)	10.0 (fixed)	–	-0.9	10.0
u_{115}	H(7)...O(11)	336.5(6)	9.9 (fixed)	–	-1.0	9.9
u_{114}	H(10)...O(11)	336.5(6)	9.9 (fixed)	–	-1.0	9.9
u_{116}	N(1)...H(15)	341.3(6)	10.0 (fixed)	–	-0.9	10.0
u_{117}	N(1)...H(13)	341.3(6)	10.0 (fixed)	–	-0.9	10.0
u_{118}	H(12)...H(15)	353.2(17)	16.6 (fixed)	–	-1.2	16.6
u_{119}	H(13)...H(14)	353.2(17)	16.6 (fixed)	–	-1.2	16.6
u_{120}	C(2)...H(17)	357.4(7)	11.5 (fixed)	–	-1.7	11.5
u_{121}	C(3)...H(18)	357.4(7)	11.4 (fixed)	–	-1.7	11.4
u_{122}	H(6)...H(10)	362.9(13)	16.8 (fixed)	–	-1.3	16.8
u_{123}	H(7)...H(9)	362.9(13)	16.8 (fixed)	–	-1.3	16.8
u_{125}	H(13)...H(19)	367.6(9)	16.7 (fixed)	–	-1.2	16.7
u_{124}	H(15)...H(19)	367.6(9)	16.7 (fixed)	–	-1.2	16.7

u_{128}	C(5)...H(10)	375.6(8)	10.7 (fixed)	–	-1.3	10.7
u_{129}	H(7)...C(8)	375.6(8)	10.7 (fixed)	–	-1.3	10.7
u_{126}	C(2)...H(13)	375.9(7)	10.6 (fixed)	–	-1.3	10.6
u_{127}	C(3)...H(15)	375.9(7)	10.6 (fixed)	–	-1.3	10.6
u_{130}	H(9)...H(17)	380.8(9)	18.1 (fixed)	–	-2.3	18.1
u_{131}	H(6)...H(18)	380.8(9)	18.1 (fixed)	–	-2.3	18.1
u_{132}	H(7)...H(18)	382.1(9)	17.5 (fixed)	–	-1.9	17.5
u_{133}	H(10)...H(17)	382.1(9)	17.5 (fixed)	–	-1.9	17.5
u_{134}	H(9)...H(12)	388.3(10)	17.3 (fixed)	–	-1.7	17.3
u_{135}	H(6)...H(14)	388.3(10)	17.3 (fixed)	–	-1.7	17.3
u_{136}	B(4)...C(8)	396.2(9)	12.1(5)	8.3(8)	-0.7	8.3
u_{137}	B(4)...C(5)	396.2(9)	12.1 (Tied to u136)	–	-0.7	8.3
u_{141}	H(10)...H(12)	397.1(15)	20.7 (fixed)	–	-1.4	20.7
u_{140}	H(7)...H(14)	397.1(15)	20.7 (fixed)	–	-1.4	20.7
u_{142}	H(13)...H(15)	397.6(16)	13.5 (fixed)	–	-1.7	13.5
u_{138}	H(9)...H(13)	398.0(12)	20.8 (fixed)	–	-1.5	20.6
u_{139}	H(6)...H(15)	398.0(12)	20.8 (fixed)	–	-1.5	20.8
u_{143}	H(7)...H(10)	413.5(9)	13.6 (fixed)	–	-1.7	13.6
u_{144}	C(5)...H(17)	423.4(11)	17.4 (fixed)	–	-0.8	17.4
u_{145}	C(8)...H(18)	423.4(11)	17.4 (fixed)	–	-0.8	17.4
u_{146}	C(8)...H(16)	425.2(12)	18.2 (fixed)	–	-1.2	18.2
u_{147}	C(5)...H(16)	425.2(12)	18.2 (fixed)	–	-1.2	18.2
u_{148}	B(4)...H(14)	428.3(11)	16.8 (fixed)	–	-1.0	16.8
u_{149}	B(4)...H(12)	428.3(11)	16.8 (fixed)	–	-1.0	16.8
u_{152}	H(12)...H(17)	442.0(15)	23.6 (fixed)	–	-0.6	23.6
u_{151}	H(14)...H(18)	442.0(15)	23.6 (fixed)	–	-0.6	23.6
u_{150}	B(4)...O(11)	442.2(7)	11.9(5)	–	-1.0	9.5

u_{153}	O(11)...H(16)	454.2(14)	20.2 (fixed)	–	-1.0	20.2
u_{157}	C(5)...H(18)	473.9(10)	13.0 (fixed)	–	-2.3	13.0
u_{156}	C(8)...H(17)	473.9(10)	13.0 (fixed)	–	-2.3	13.0
u_{155}	B(4)...H(15)	475.0(9)	12.8 (fixed)	–	-1.4	12.8
u_{154}	B(4)...H(13)	475.0(9)	12.8 (fixed)	–	-1.4	12.8
u_{158}	H(10)...H(13)	477.4(7)	12.5 (fixed)	–	-2.5	12.5
u_{159}	H(7)...H(15)	477.4(7)	12.5 (fixed)	–	-2.5	12.5
u_{160}	H(14)...H(16)	482.4(12)	19.6 (fixed)	–	-2.6	19.6
u_{161}	H(12)...H(16)	482.4(12)	19.6 (fixed)	–	-2.6	19.6
u_{162}	H(13)...H(16)	489.1(14)	24.2 (fixed)	–	-1.6	24.2
u_{163}	H(15)...H(16)	489.1(14)	24.2 (fixed)	–	-1.6	24.2
u_{165}	H(15)...H(18)	489.6(12)	21.6 (fixed)	–	-1.2	21.6
u_{164}	H(13)...H(17)	489.6(12)	21.6 (fixed)	–	-1.2	21.6
u_{166}	H(14)...H(17)	491.8(14)	22.6 (fixed)	–	-2.1	22.6
u_{167}	H(12)...H(18)	491.8(14)	22.6 (fixed)	–	-2.1	22.6
u_{168}	O(11)...H(18)	501.3(9)	15.4 (fixed)	–	-2.2	15.4
u_{169}	O(11)...H(17)	501.3(9)	15.4 (fixed)	–	-2.2	15.4
u_{170}	H(15)...H(17)	564.2(10)	14.8 (fixed)	–	-3.7	14.8
u_{171}	H(13)...H(18)	564.2(10)	14.7 (fixed)	–	-3.7	14.7

[A] All values are tabulated in picometers (pm).

Table S15: Refined (r_{h1}) and calculated (r_e) geometric parameters for the GED refinement of **MBC**.

	Parameter[A]	MP2/6-311+G* (r_e)	SARACEN (r_{h1})	Restraint
p_1	*r*B-H average	121.5	121.5(4)	121.5(3)
p_2	*r*B-N	163.2	164.4(6)	163.2(9)
p_3	*r*N-C	148.3	148.2(2)	148.3(2)
p_4	*r*N-H	102.2	102.2(7)	102.2(6)
p_5	*r*C-C	151.8	152.0(6)	–
p_6	*r*O...N	287.9	291.2(4)	287.9(5)
p_7	*r*C-H average	109.4	109.4(1)	109.4(1)
p_8	∠N-B-H average	105.4	105.3(4)	105.4(3)
p_9	∠C(6)-N(5)-B(1)	112.6	113.6(3)	–
p_{10}	∠C(8)-C(6)-N(5)	111.2	111.2(2)	111.2(2)
p_{11}	∠O(10)...N(5)-B(1)	153.0	153.6(5)	153.0(5)
p_{12}	∠H-(N/C)-(B/N/C) average	108.2	107.7(4)	108.2(3)
p_{13}	ϕC(6)-N(5)-B(1)-H(2)	62.0	62.0(4)	62.0(3)
p_{14}	ϕC(8)-C(6)-N(5)-B(1)	–178.8	–180.3(5)	–178.8(6)
p_{15}	ϕH(12)-C(6)-N(5)-B(1)	-58.1	-58.1(3)	-58.1(3)
p_{16}	ϕH(13)-C(6)-N(5)-B(1)	58.0	58.2(4)	58.0(3)
p_{17}	ϕH(16)-C(8)-C(6)-N(5)	175.6	175.6(4)	175.6(3)
p_{18}	ϕH(17)-C(8)-C(6)-N(5)	–64.8	-64.8(4)	–64.8(3)

d_1	rC–O	141.8	142.8(5)	–

[A] Distances in pm, bond angles and torsion angles in °. Figures in parentheses are the estimated standard deviation of the last digits.

Figure S1: Experimental and final weighted difference (experimental – theoretical) molecular intensity curves for the GED refinement of **MBC**. L indicates data from the long nozzle-to-camera distance, S indicates data from the short nozzle-to-camera distance.