Electronic Supplementary Information (ESI)

Equilibrium molecular structure and spectra of 6-methyl-1,5-diazabicyclo[3.1.0]hexane: joint analysis of gas-phase electron diffraction, quantum chemistry, and spectroscopic data

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Contents

1. Synthesis of 6-methyl-1,5-diazabicyclo[3.1.0]hexane (MDABH) and mass spectra

MDABH was synthesized in the N. D. Zelinsky Institute of Organic Chemistry, RAS.

Acetaldehyde (2.5 g, 50 mmol) in H_2O (10 ml) was added dropwise to a stirred solution of 1,3-diaminopropane (3.7 g, 50 mmol) in H_2O (50 ml) at a temperature of 0–10 °C. Then pH of the reaction mixture was brought to 11.0 by addition of 15% aqueous HCl. Then a 12% aqueous solution of NaOCl (30 ml, 50 mmol) was slowly added dropwise at a temperature of 0–5 °C and pH of 11.5–12.0. The reaction mixture was stirred for 12 h at 0–5° C and pH of 11.5–12.0, which was maintained by addition of 20% aqueous NaOH if necessary. The temperature was raised to 20 °C, and the mixture was saturated with NaCl and extracted with $CHCl_3$ (50 ml × 4); the organic layers were dried over K_2CO_3, and the solvent was evaporated in vacuo. The resulting residue was distilled at a reduced pressure to yield a light liquid. Bp: 64−66 °C (15 Torr). Yield 3.7 g (75.5%).

Mass spectra were measured using a Finnigan MAT INCOS-50 instrument. High resolution mass spectra were recorded on an electrospray ionization (ESI) Bruker microTOF spectrometer. All measurements were performed in a positive (+MS) ion mode (interface capillary voltage: 4500 V) with m/z scan range of 50-3000. HRMS (ESI): m/z for $C_5H_{11}N_2$ $(M+H)^+$: calcd 99.0917, found 99.0921; Mass-spectra (EI, 70 eV), m/z: 98 (44) $[M]^+$, 97 (100) $[M - H]^+$, 83 (3) $[M - Me]^+$, 70 (20) $[M – (\text{-}CH_2\text{-})_2]^+$, 69 (75) $[M – (\text{-}CH_2\text{-})_2 - H]^+$, 56 (19) $[M – (\text{-}CH_2\text{-})_3]^+$, 55 (10) $[M – (\text{-}CH_2\text{-})_3 - H]^+$, 42 (39) $[(\text{-}CH_2\text{-})_3]^+$, 41 (18) $[(\text{-}CH_2\text{-})_3 - H]^+$, 28 (21) $[(\text{-}CH_2\text{-})_2]^+$, 27 (10) $[(\text{-}CH_2\text{-})_2 - H]^+$, 26 (5) $[(\text{-}CH_2\text{-})_2 - 2H]^+$.

2. NMR spectra

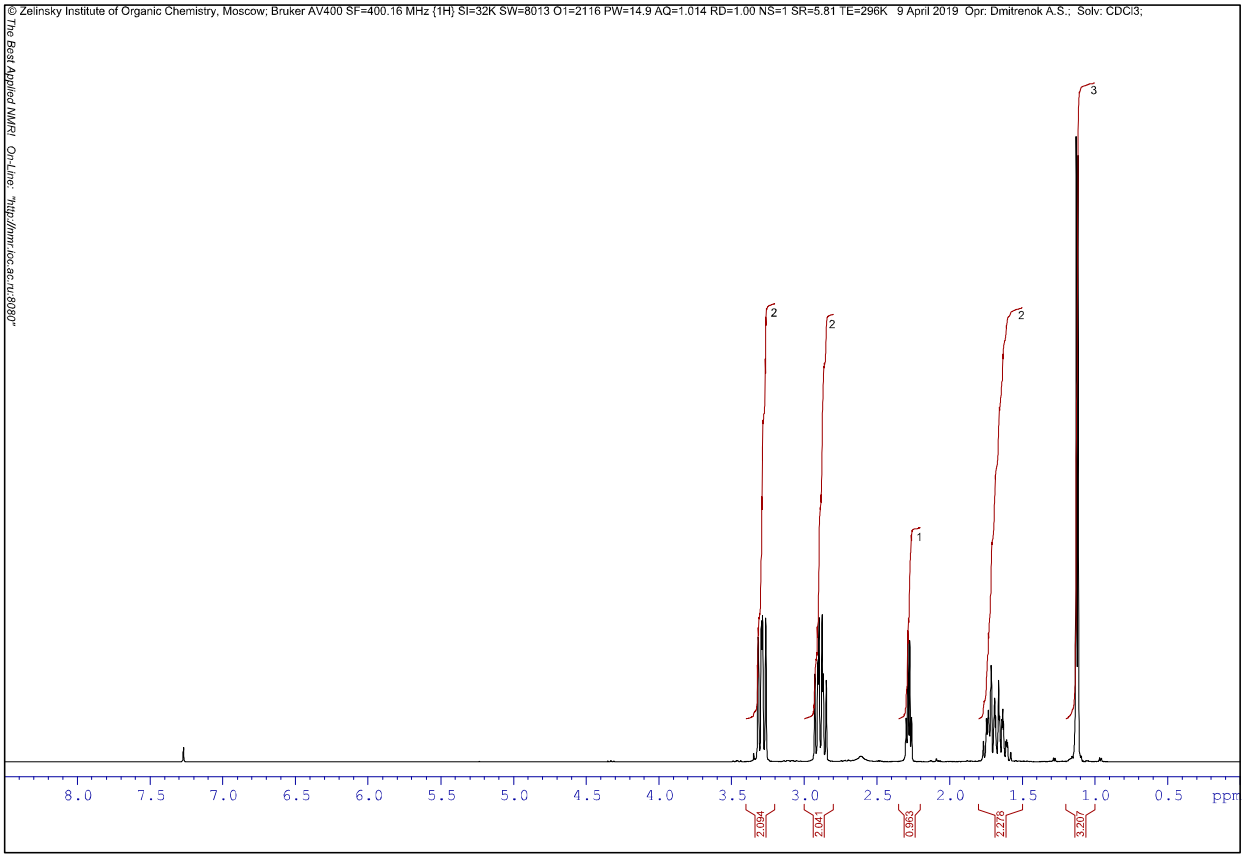

Fig. S1. ^{1}H NMR spectrum of MDABH ($CDCl_3$)

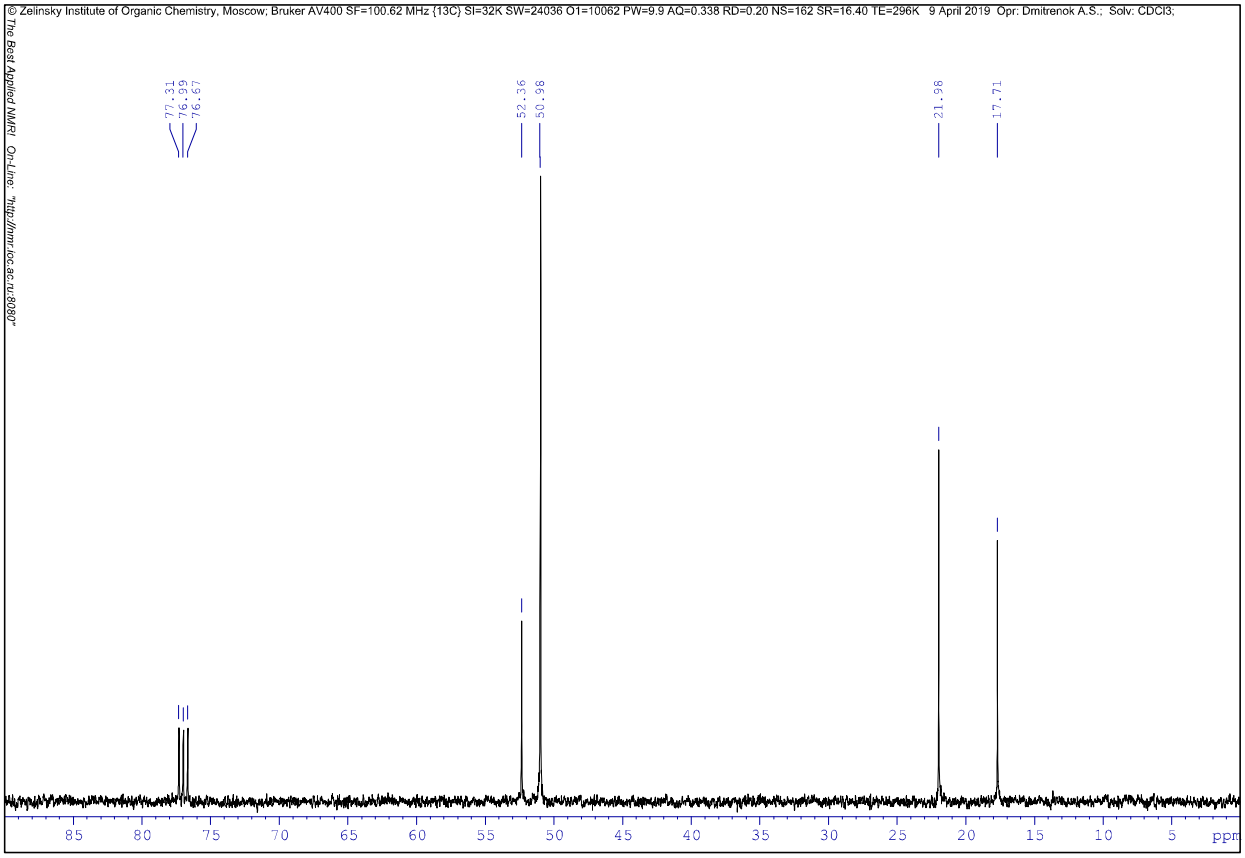

Fig. S2. ^{13}C NMR spectrum of MDABH ($CDCl_3$)

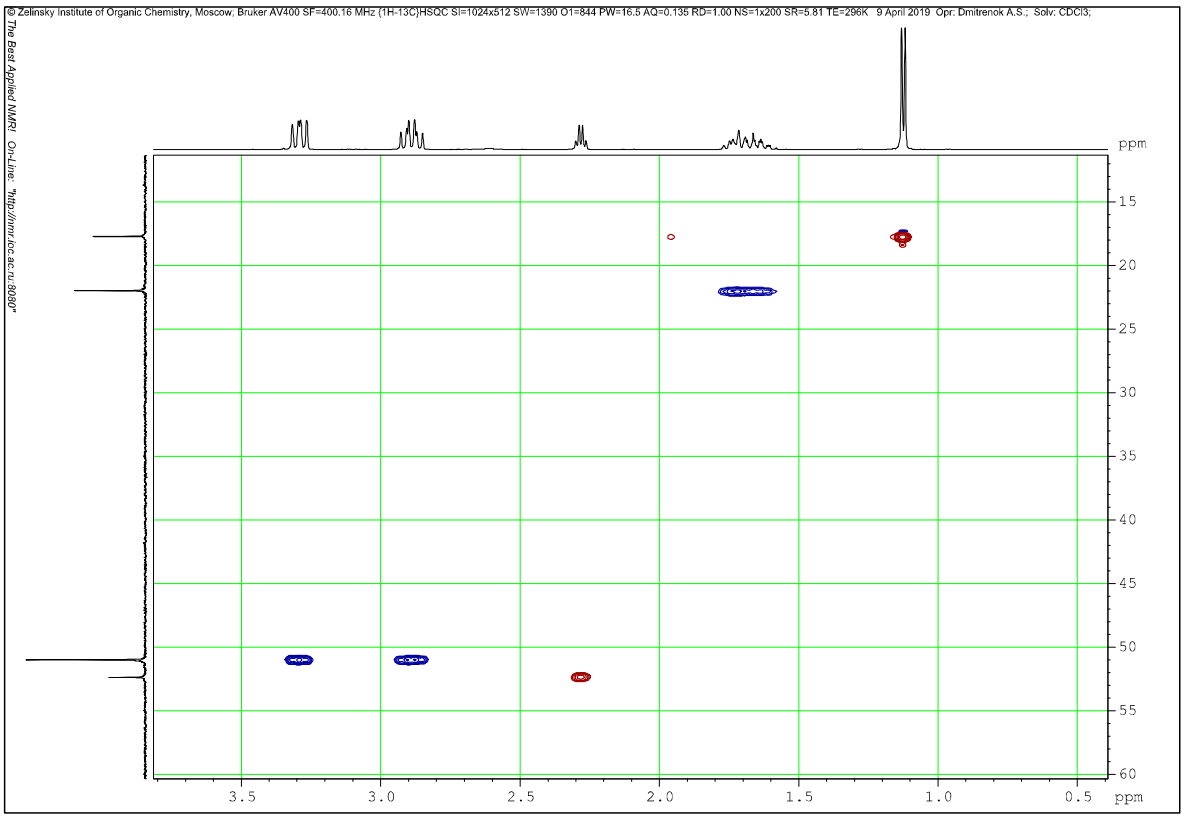

Fig. S3. {^{1}H-^{13}C} HSQC spectrum of MDABH ($CDCl_3$)

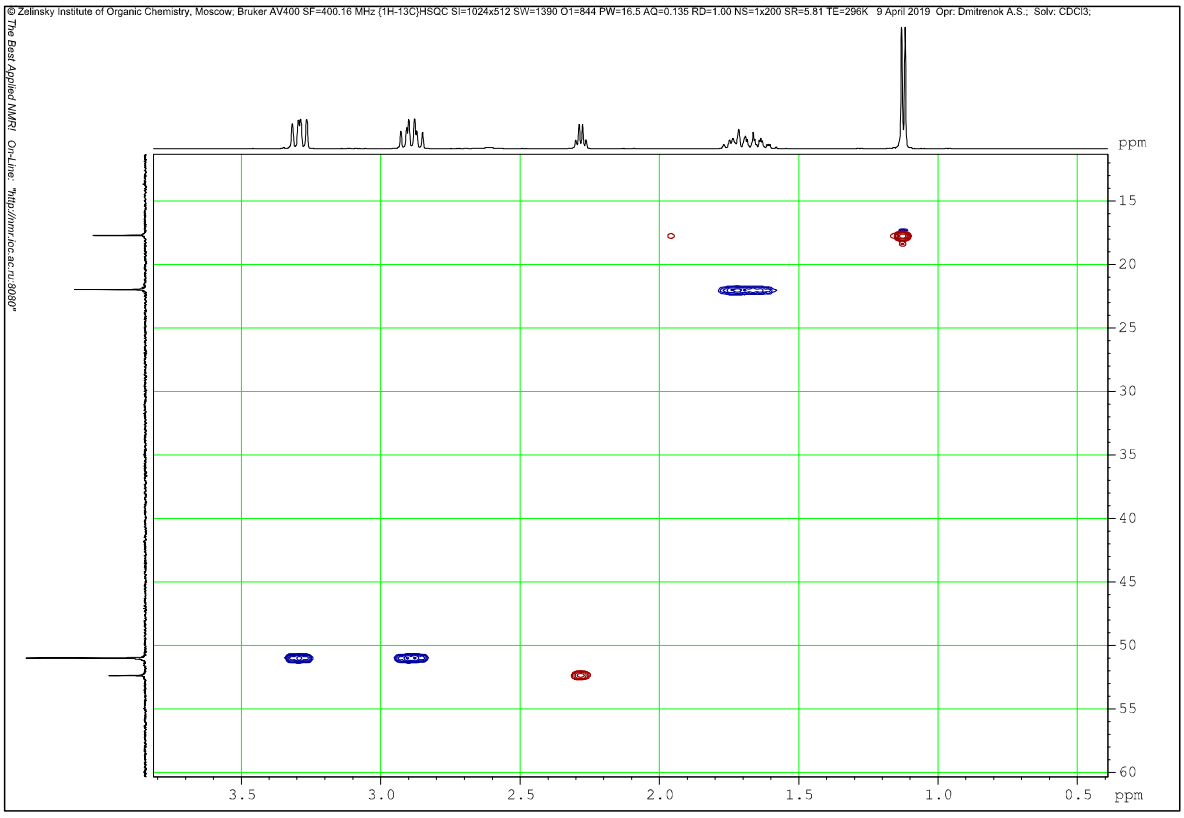

Fig. S4. {^{1}H-^{13}C} HMBC spectrum of MDABH ($CDCl_3$)

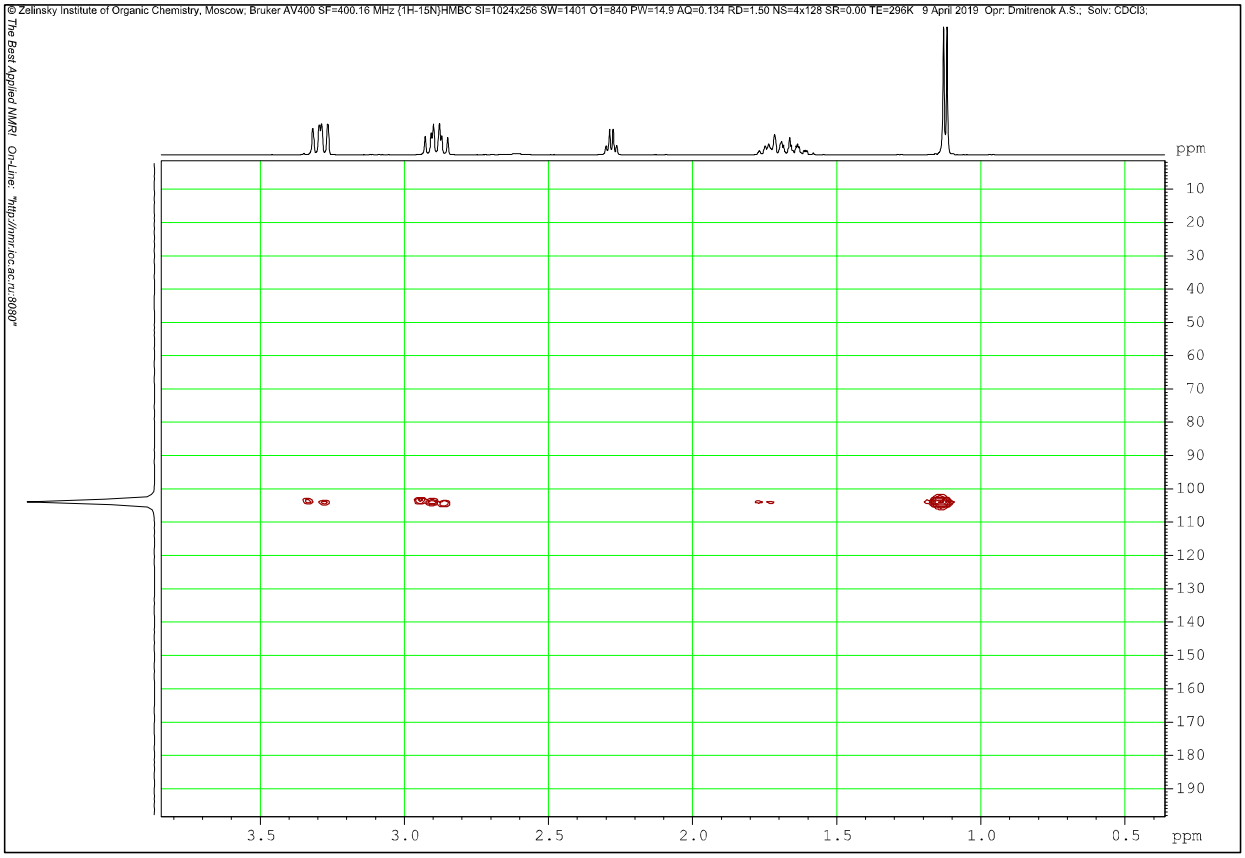

Fig. S5. {^{1}H-^{15}N} HMBC spectrum of MDABH ($CDCl_3$)

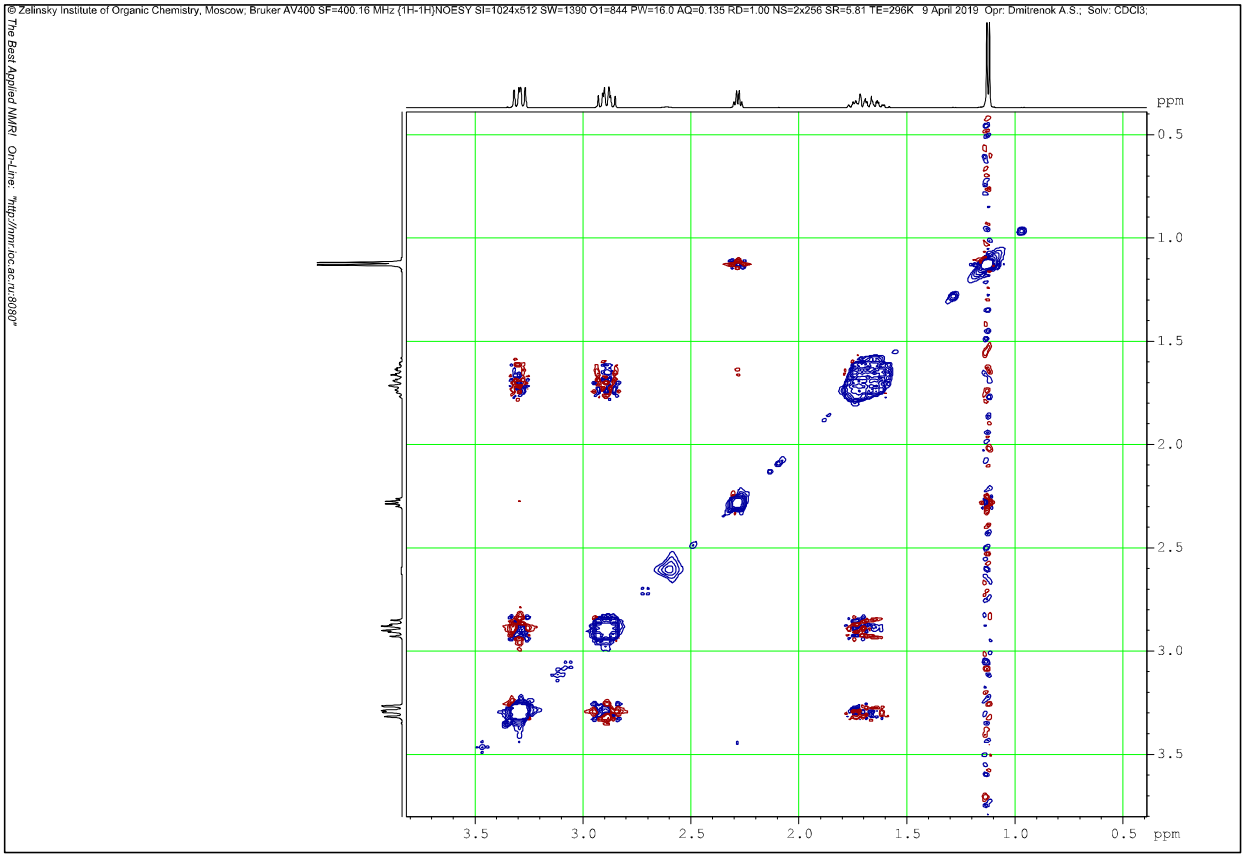

Fig. S6. {^{1}H-^{1}H}gNOESY spectrum of MDABH ($CDCl_3$).

3. IR and Raman spectra

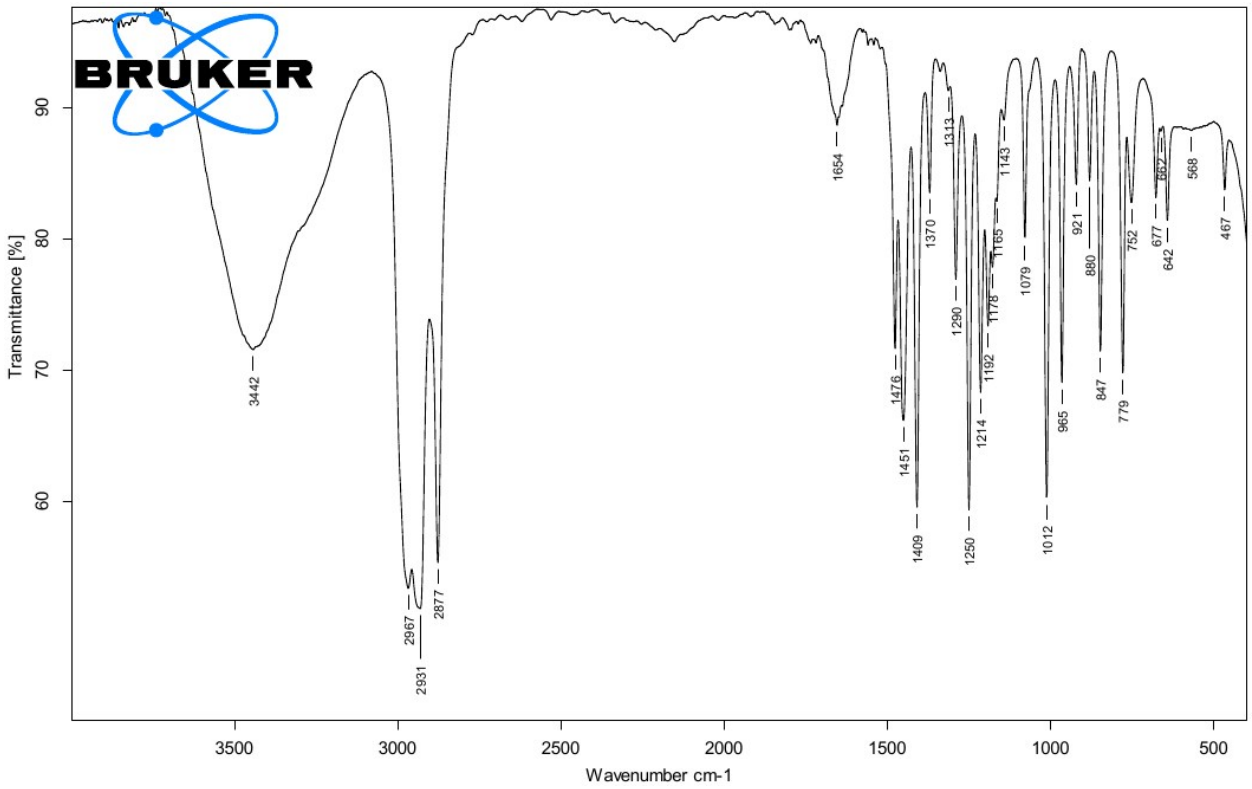

Figure S7 IR spectrum of 6-methyl-1,5-diazabicyclo[3.1.0]hexane (MDABH).

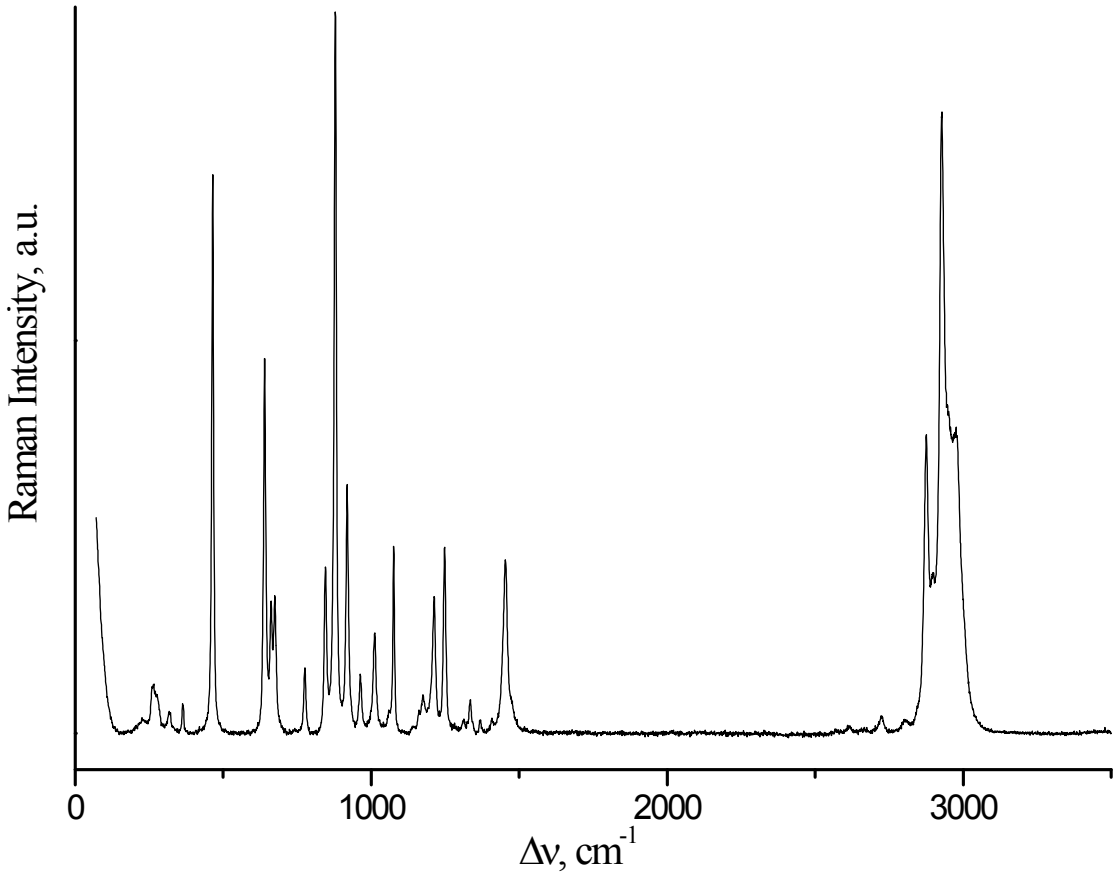

Figure S8 Raman spectrum of 6-methyl-1,5-diazabicyclo[3.1.0]hexane (MDBH) (total)

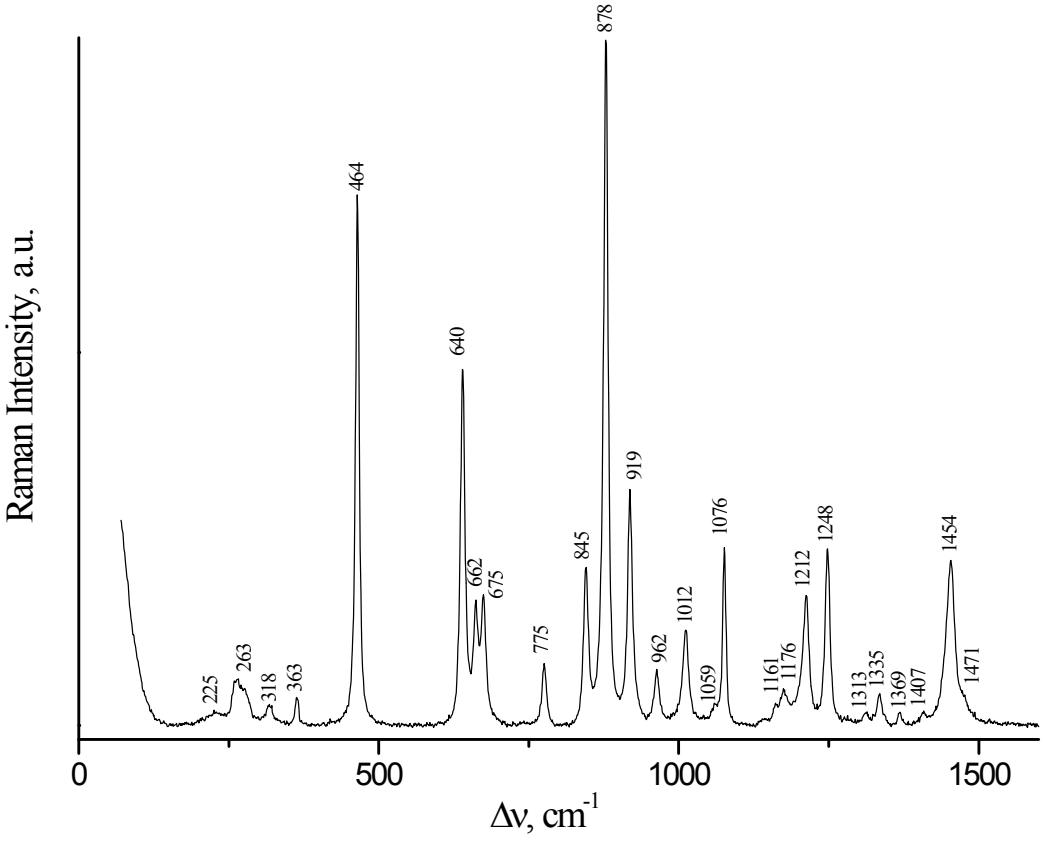

Figure S9 Raman spectrum of 6-methyl-1,5-diazabicyclo[3.1.0]hexane (MDABH) (part 1).

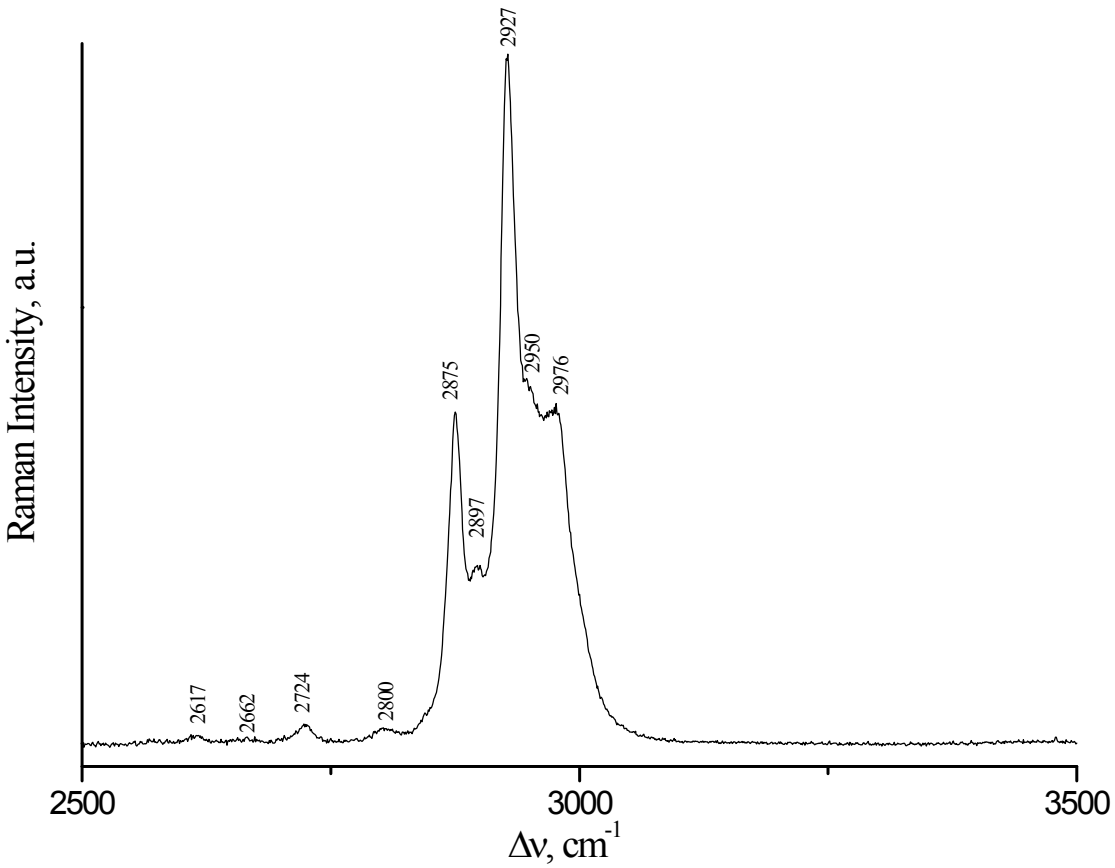

Figure S10 Raman spectrum of 6-methyl-1,5-diazabicyclo[3.1.0]hexane (MDABH) (part 2)

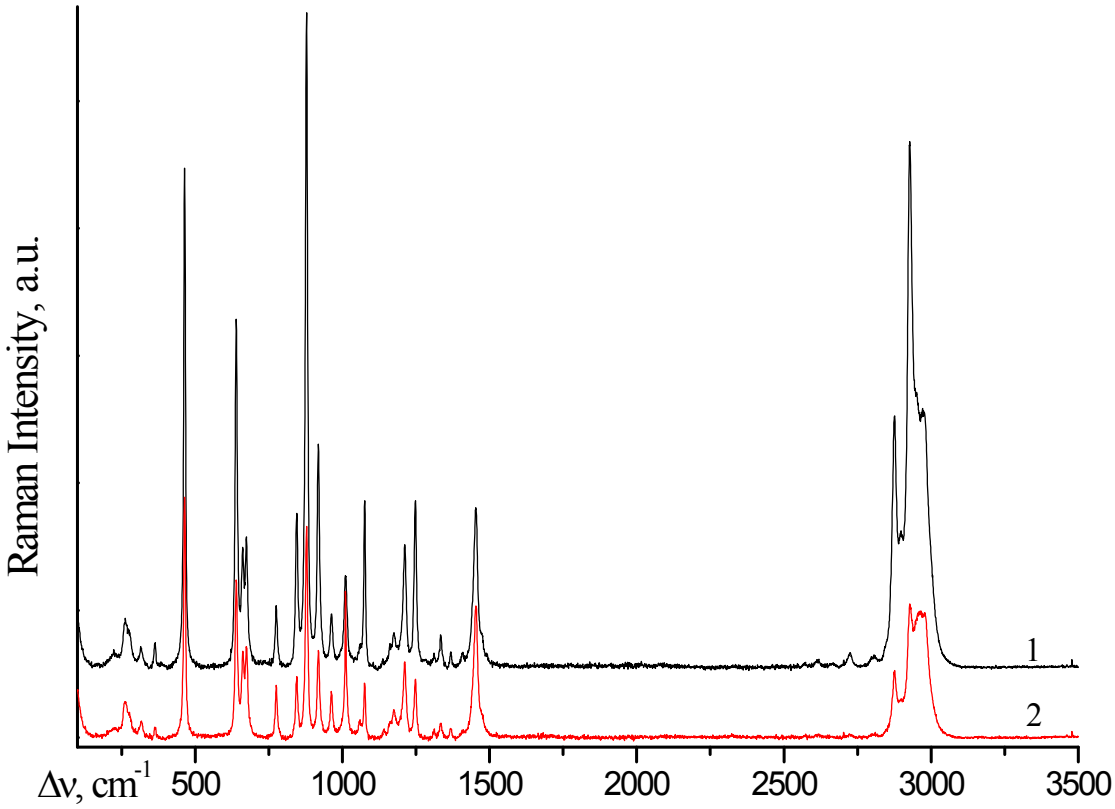

Fig.S11 Depolarized (1) and polarized (2) Raman spectra of 6-methyl-1,5-diazabicyclo[3.1.0]hexane

Table S1. Redundant set of internal vibrational coordinates for the MDABH molecule.

No.	Notation	Atom group	No.	Notation	Atom group
Stretching coordinates			***Bending coordinates***		
1	NN	N1–N5	1	H9C2H10	H9–C2–H10
2	N1C2	N1–C2	2	N1C2H9	N1–C2–H9
3	C4N5	C4–N5	3	N1C2H10	N1–C2–H10
4	C6N5	C6–N5	4	C3C2H9	C3–C2–H9
5	N5C6	N5–C6	5	C3C2H10	C3–C2–H10
6	C2C3	C2–C3	6	H13C4H14	H13–C4–H14
7	C3C4	C3–C4	7	N5C4H13	N5–C4–H13
8	C6C7	C6–C7	8	N5C4H14	N5–C4–H14
9	C2H9	C2–H9	9	C3C4H13	C3–C4–H13
10	C2H10	C2–H10	10	C3C4H14	C3–C4–H14
11	C3H11	C3–H11	11	H11C3H12	H11–C3–H12
12	C3H12	C3–H12	12	C2C3H11	C2–C3–H11
13	C4H13	C4–H13	13	C4C3H11	C4–C3–H11
14	C4H14	C4–H14	14	C2C3H12	C2–C3–H12
15	C6H8	C6–H8	15	C4C3H12	C4–C3–H12
16	C7H15	C7–H15	16	C2C3C4	C2–C3–C4
17	C7H16	C7–H16	17	N1C2C3	N1–C2–C3
18	C7H17	C7–H17	18	C3C4N5	C3–C4–N5
			19	N1N5C4	N1–N5–C4
Torsional coordinates			20	C2N1N5	C2–N1–N5
1	C6N1N5C4	(C6)N1–N5(C4)	21	N1N5C6	N1–N5–C6
2	C6N5N1C2	(C6)N5–N1(C2)	22	N5N1C6	N5–N1–C6
3	N1C2C3C4	(N1)C2–C3(C4)	23	N1C6N5	N1–C6–N5
4	N5C4C3C2	(N5)C4–C3(C2)	24	H8C6C7	H8–C6–C7
5	N5N1C2C3	(N5)N1–C2(C3)	25	H8C6N1	H8–C6–N1
6	N1N5C4C3	(N1)N5–C4(C3)	26	H8C6N5	H8–C6–N5
7	C2N1N5C4	(C2)N1–N5(C4)	27	N5C6C7	N5–C6–C7
8	CC_{Me} torsion	(N1,N5)C6–C7(H15,H16,H17)	28	N1C6C7	N1–C6–C7
			29	C6C7H15	C6–C7–H15
			30	C6C7H16	C6–C7–H16
			31	C6C7H17	C6–C7–H17
			32	H15C7H16	H15–C7–H16
			33	H15C7H17	H15–C7–H17
			34	H16C7H17	H16–C7–H17

4. Results of quantum chemical calculations

Table S2. Cartesian coordinates of the boat form of MDABH found by the MP2(full)/aug-cc-pVTZ calculation

Atom	X	Y	Z
N1	1.4290924678	-0.7569955034	1.1400845933
C2	0.0259254118	-1.1845756349	1.077351326
C3	-0.8125989867	0.	0.6084901472
C4	0.0259254118	1.1845756349	1.077351326
N5	1.4290924678	0.7569955034	1.1400845933
C6	1.8203640201	0.	-0.0235451748
C7	3.2683553839	0.	-0.3703353045
H8	1.1294488909	0.	-0.8588613605
H9	-0.2570030251	-1.4849727007	2.0832104978
H10	-0.0489418145	-2.0494680648	0.421152907
H11	-0.9393682502	0.	-0.4691716677
H12	-1.8007451274	0.	1.0585606465
H13	-0.2570030251	1.4849727007	2.0832104978
H14	-0.0489418145	2.0494680648	0.421152907
H15	3.8473632312	0.	0.547701875
H16	3.5200598564	-0.8846315724	-0.9516421789
H17	3.5200598564	0.8846315724	-0.9516421789

Table S3. Cartesian coordinates of the chair form of MDABH found by the MP2(full)/aug-cc-pVTZ calculation.

Atom	X	Y	Z
N1	1.413166	-0.770074	1.000087
C2	0.000000	-1.185976	1.000006
C3	-0.778023	0.	1.544777
C4	0.000000	1.185976	1.000034
N5	1.413166	0.770074	1.000000
C6	1.758744	0.	-0.167665
C7	3.186440	0.	-0.589895
H8	1.019795	0.	-0.964180
H9	-0.085144	-2.062871	1.634279
H10	-0.332180	-1.446145	-0.005982
H11	-1.821680	0.	1.239444
H12	-0.728441	0.	2.631056
H13	-0.085144	2.062871	1.634279
H14	-0.332180	1.446145	-0.005982
H15	3.812102	0.	0.297061
H16	3.406307	-0.885169	-1.183214
H17	3.406307	0.885169	-1.183214

Table S4. Cartesian coordinates of the boat form of MDABH found by the B3LYP/aug-cc-pVTZ calculation.

Atom	X	Y	Z
N1	1.4186290909	-0.7546860775	1.1367605802
C2	0.0121184361	-1.1984573903	1.0710228714
C3	-0.8464340245	0.	0.6339481918
C4	0.0121184361	1.1984573903	1.0710228714
N5	1.4186290909	0.7546860775	1.1367605802
C6	1.8411037727	0.	-0.022855918
C7	3.3028000824	0.	-0.3655816629
H8	1.1715752927	0.	-0.8808634645
H9	-0.2603650874	-1.5339467838	2.0717194923
H10	-0.0652120016	-2.0525664542	0.3970834037
H11	-1.0173743537	0.	-0.4411075954
H12	-1.8231380797	0.	1.1144570636
H13	-0.2603650874	1.5339467838	2.0717194923
H14	-0.0652120016	2.0525664542	0.3970834037
H15	3.8960800854	0.	0.5463775087
H16	3.5580656506	-0.8844671796	-0.9521966845
H17	3.5580656506	0.8844671796	-0.9521966845

Table S5. Cartesian coordinates of the chair form of MDABH found by the B3LYP/aug-cc-pVTZ calculation.

Atom	X	Y	Z
N1	1.4214927515	-0.7631292003	1.0042215375
C2	0.0066987308	-1.2048748627	1.0109520342
C3	-0.812973493	0.	1.4876652734
C4	0.0066987308	1.2048748627	1.0109520342
N5	1.4214927515	0.7631292003	1.0042215375
C6	1.7832627285	0.	-0.1679502176
C7	3.2204004286	0.	-0.6021365906
H8	1.0569521956	0.	-0.9815457082
H9	-0.0760225562	-2.0513775665	1.6900231157
H10	-0.3039577629	-1.5361829042	0.0165020939
H11	-1.8300500602	0.	1.0965997393
H12	-0.8722117708	0.	2.5761088271
H13	-0.0760225562	2.0513775665	1.6900231157
H14	-0.3039577629	1.5361829042	0.0165020939
H15	3.8695595713	0.	0.2710000537
H16	3.4374726437	-0.8848379125	-1.2033828884
H17	3.4374726437	0.8848379125	-1.2033828884

4. Experimental GED data for structural analysis and refinement results

Table S6 GED experimental conditions for the long (LD) and short (SD) camera distances

Parameter	LD= 362.3 mm	SD= 193.9 mm
Beam current, μA	1.7	1.6
Exposure time, s	35	70
Nozzle temperature, K	293	293
Residual gas pressure, mm Hg	2.510^{-5}	$3.0 \cdot 10^{-5}$
Number of the diffraction patterns for the substance	3	2
Number of the diffraction patterns for the standard (CCl_4)	2	2
Wavelength of electrons (λ), Å	0.0496746	0.0498963
Interval of scattering angles (s), $Å^{-1}$	3.375–16.750 (Δs=0.125)	7.75–29.75 (Δs=0.25)

Table S7. Total scattering intensity functions $I^{tot}(s)$ and the background lines $I^{b}(s)$ for MDABH. Long camera distance (LD=362.3 mm).

Diffraction pattern 1

S	$I^{tot}(s)$	$I^{b}(s)$	s	$I^{tot}(s)$	$I^{b}(s)$	s	$I^{tot}(s)$	$I^{b}(s)$
3.375	0.536311	0.567310	7.875	0.504949	0.524406	12.375	0.406909	0.416351
3.500	0.542346	0.569734	8.000	0.510658	0.520361	12.500	0.408193	0.414347
3.625	0.542063	0.575172	8.125	0.515922	0.516318	12.625	0.409903	0.412333
3.750	0.538505	0.582436	8.250	0.520010	0.512264	12.750	0.412349	0.410331
3.875	0.534846	0.590576	8.375	0.522876	0.508200	12.875	0.415062	0.408359
4.000	0.533670	0.598853	8.500	0.523657	0.504157	13.000	0.417466	0.406417
4.125	0.539230	0.606676	8.625	0.522789	0.500104	13.125	0.419560	0.404517
4.250	0.549091	0.613597	8.750	0.519888	0.496090	13.250	0.421028	0.402666
4.375	0.563062	0.619297	8.875	0.515232	0.492116	13.375	0.421629	0.400886
4.500	0.579728	0.623576	9.000	0.509431	0.488182	13.500	0.421131	0.399196
4.625	0.598275	0.626365	9.125	0.503074	0.484317	13.625	0.419455	0.397595
4.750	0.615001	0.627677	9.250	0.496552	0.480523	13.750	0.416488	0.396105
4.875	0.631485	0.627582	9.375	0.489399	0.476819	13.875	0.412260	0.394725
5.000	0.649413	0.626240	9.500	0.483035	0.473206	14.000	0.407426	0.393474
5.125	0.663494	0.623810	9.625	0.476891	0.469702	14.125	0.402280	0.392344
5.250	0.674357	0.620485	9.750	0.471129	0.466320	14.250	0.396954	0.391343
5.375	0.680965	0.616452	9.875	0.466337	0.463058	14.375	0.391880	0.390473
5.500	0.684293	0.611902	10.000	0.461854	0.459917	14.500	0.387692	0.389713
5.625	0.682701	0.606985	10.125	0.458114	0.456906	14.625	0.383920	0.389053
5.750	0.676615	0.601849	10.250	0.454324	0.454006	14.750	0.381168	0.388473
5.875	0.666672	0.596584	10.375	0.450821	0.451236	14.875	0.379175	0.387961
6.000	0.653060	0.591300	10.500	0.447548	0.448588	15.000	0.377940	0.387471
6.125	0.636258	0.586085	10.625	0.444233	0.446039	15.125	0.377152	0.386999
6.250	0.617275	0.580950	10.750	0.440341	0.443582	15.250	0.376890	0.386471
6.375	0.597606	0.575942	10.875	0.436420	0.441235	15.375	0.376570	0.385888
6.500	0.576429	0.571083	11.000	0.432136	0.438967	15.500	0.376213	0.385205
6.625	0.555889	0.566372	11.125	0.427725	0.436759	15.625	0.375955	0.384392
6.750	0.537951	0.561809	11.250	0.423451	0.434611	15.750	0.375611	0.383449
6.875	0.522622	0.557365	11.375	0.419840	0.432511	15.875	0.375151	0.382346
7.000	0.510085	0.553049	11.500	0.416116	0.430451	16.000	0.374672	0.381131
7.125	0.500921	0.548813	11.625	0.412859	0.428429	16.125	0.374343	0.379866
7.250	0.495366	0.544666	11.750	0.410559	0.426406	16.250	0.373853	0.378613
7.375	0.492498	0.540569	11.875	0.408475	0.424392	16.375	0.373681	0.377528
7.500	0.492613	0.536503	12.000	0.407317	0.422387	16.500	0.373610	0.376796
7.625	0.495096	0.532466	12.125	0.406612	0.420372	16.625	0.373693	0.376706
7.750	0.499492	0.528431	12.250	0.406519	0.418366	16.750	0.373834	0.377616

Diffraction pattern 2

s	$I^{tot}(s)$	$I^{b}(s)$	S	$I^{tot}(s)$	$I^{b}(s)$	s	$I^{tot}(s)$	$I^{b}(s)$
3.375	0.537697	0.568631	7.875	0.505829	0.525436	12.375	0.407877	0.417347
3.500	0.543627	0.571256	8.000	0.511609	0.521402	12.500	0.409177	0.417347
3.625	0.543317	0.576718	8.125	0.517003	0.517363	12.625	0.410812	0.415365
3.750	0.539852	0.583881	8.250	0.521005	0.513325	12.750	0.413352	0.413371
3.875	0.536106	0.591876	8.375	0.523874	0.509289	12.875	0.416027	0.411400
4.000	0.534978	0.599953	8.500	0.524708	0.505231	13.000	0.418431	0.409444
4.125	0.540107	0.607570	8.625	0.523860	0.501213	13.125	0.420510	0.407501
4.250	0.549679	0.614296	8.750	0.520948	0.497205	13.250	0.422169	0.405606
4.375	0.563821	0.619838	8.875	0.516517	0.493233	13.375	0.422817	0.403758
4.500	0.580122	0.623987	9.000	0.510580	0.489307	13.500	0.422341	0.401961
4.625	0.598622	0.626694	9.125	0.504225	0.485447	13.625	0.420697	0.400236
4.750	0.615315	0.627956	9.250	0.497640	0.481655	13.750	0.417676	0.398593
4.875	0.632084	0.627852	9.375	0.490633	0.477941	13.875	0.413398	0.397040
5.000	0.649622	0.626533	9.500	0.483998	0.474320	14.000	0.408340	0.395606
5.125	0.663892	0.624155	9.625	0.477990	0.470814	14.125	0.403025	0.394268
5.250	0.674765	0.620909	9.750	0.472276	0.467411	14.250	0.397557	0.393057
5.375	0.681467	0.616951	9.875	0.467433	0.464136	14.375	0.392320	0.391944
5.500	0.684681	0.612473	10.000	0.462869	0.460978	14.500	0.387906	0.390966
5.625	0.683231	0.607645	10.125	0.459132	0.457931	14.625	0.384064	0.390082
5.750	0.677337	0.602573	10.250	0.455388	0.455016	14.750	0.381212	0.389303
5.875	0.667525	0.597387	10.375	0.451815	0.452223	14.875	0.379052	0.388605
6.000	0.653952	0.592167	10.500	0.448533	0.449540	15.000	0.377635	0.387979
6.125	0.637111	0.586985	10.625	0.445194	0.446966	15.125	0.376964	0.387381
6.250	0.618340	0.581891	10.750	0.441292	0.444508	15.250	0.376623	0.386813
6.375	0.598548	0.576910	10.875	0.437322	0.442127	15.375	0.376321	0.386225
6.500	0.577390	0.572074	11.000	0.433008	0.439834	15.500	0.376080	0.385583
6.625	0.556714	0.567371	11.125	0.428601	0.437626	15.625	0.375742	0.384877
6.750	0.538791	0.562816	11.250	0.424356	0.435472	15.750	0.375427	0.384077
6.875	0.523593	0.558388	11.375	0.420742	0.433373	15.875	0.375012	0.383155
7.000	0.511160	0.554051	11.500	0.416984	0.431315	16.000	0.374520	0.382121
7.125	0.502012	0.549826	11.625	0.413738	0.429289	16.125	0.374241	0.380990
7.250	0.496440	0.545673	11.750	0.411331	0.427271	16.250	0.373787	0.379804
7.375	0.493671	0.541570	11.875	0.409297	0.425283	16.375	0.373586	0.378622
7.500	0.493774	0.537516	12.000	0.408296	0.423305	16.500	0.373615	0.377583
7.625	0.496198	0.533488	12.125	0.407563	0.421313	16.625	0.373591	0.376831
7.750	0.500395	0.529457	12.250	0.407431	0.419337	16.750	0.373576	0.376610

Diffraction pattern 3

s	$I^{tot}(s)$	$I^{b}(s)$	s	$I^{tot}(s)$	$I^{b}(s)$	s	$I^{tot}(s)$	$I^{b}(s)$
3.375	0.497890	0.531047	7.875	0.464062	0.482914	12.375	0.381925	0.390771
3.500	0.503881	0.532163	8.000	0.469685	0.479039	12.500	0.383136	0.388843
3.625	0.503131	0.536533	8.125	0.475136	0.475215	12.625	0.384951	0.386914
3.750	0.499501	0.542949	8.250	0.479218	0.471459	12.750	0.387241	0.384987
3.875	0.496338	0.550486	8.375	0.482381	0.467762	12.875	0.389502	0.383059
4.000	0.494792	0.558384	8.500	0.483618	0.464133	13.000	0.391964	0.381151
4.125	0.498630	0.566068	8.625	0.482732	0.460572	13.125	0.394093	0.379284
4.250	0.507372	0.573037	8.750	0.480268	0.457090	13.250	0.395642	0.377465
4.375	0.520578	0.578960	8.875	0.476442	0.453686	13.375	0.396299	0.375716
4.500	0.537383	0.583617	9.000	0.471099	0.450361	13.500	0.395706	0.374035
4.625	0.555989	0.586855	9.125	0.465338	0.447135	13.625	0.394013	0.372454
4.750	0.573978	0.588653	9.250	0.459412	0.444009	13.750	0.391176	0.370961
4.875	0.592475	0.589052	9.375	0.453294	0.440973	13.875	0.387233	0.369597
5.000	0.611628	0.588161	9.500	0.447757	0.438057	14.000	0.382585	0.368342
5.125	0.626999	0.586127	9.625	0.442500	0.435232	14.125	0.377535	0.367217
5.250	0.639248	0.583119	9.750	0.437735	0.432537	14.250	0.372283	0.366212
5.375	0.646386	0.579296	9.875	0.433529	0.429933	14.375	0.367192	0.365337
5.500	0.649779	0.574849	10.000	0.429950	0.427449	14.500	0.362776	0.364562
5.625	0.648223	0.569938	10.125	0.426831	0.425066	14.625	0.359041	0.363909
5.750	0.642263	0.564692	10.250	0.423530	0.422783	14.750	0.356178	0.363316
5.875	0.631364	0.559261	10.375	0.420687	0.420590	14.875	0.354046	0.362794
6.000	0.617076	0.553747	10.500	0.417779	0.418497	15.000	0.352738	0.362312
6.125	0.599126	0.548209	10.625	0.414632	0.416464	15.125	0.351784	0.361821
6.250	0.579089	0.542729	10.750	0.411109	0.414511	15.250	0.351431	0.361321
6.375	0.557393	0.537327	10.875	0.407215	0.412617	15.375	0.351161	0.360751
6.500	0.535098	0.532055	11.000	0.403390	0.410763	15.500	0.350915	0.360100
6.625	0.514488	0.526934	11.125	0.399177	0.408959	15.625	0.350654	0.359330
6.750	0.496883	0.521956	11.250	0.395238	0.407165	15.750	0.350241	0.358440
6.875	0.481456	0.517131	11.375	0.391814	0.405391	15.875	0.350106	0.357430
7.000	0.468932	0.512458	11.500	0.388624	0.403628	16.000	0.349640	0.356319
7.125	0.459935	0.507919	11.625	0.385898	0.401845	16.125	0.349545	0.355149
7.250	0.454597	0.503494	11.750	0.383920	0.400053	16.250	0.349393	0.354005
7.375	0.451705	0.499191	11.875	0.382394	0.398242	16.375	0.349194	0.353036
7.500	0.452041	0.494992	12.000	0.381496	0.396411	16.500	0.349264	0.352429
7.625	0.454615	0.490894	12.125	0.381380	0.394551	16.625	0.349353	0.352412
7.750	0.458850	0.486868	12.250	0.381413	0.392671	16.750	0.349481	0.352409

Table S8. Total scattering intensity functions $I^{tot}(s)$ and the background lines $I^{b}(s)$ for MDABH. Short camera distance (SD=193.9 mm).

Diffraction pattern 1

s	$I^{tot}(s)$	$I^{b}(s)$	s	$I^{tot}(s)$	$I^{b}(s)$	s	$I^{tot}(s)$	$I^{b}(s)$
7.75	0.572953	0.600217	15.25	0.443032	0.451227	22.75	0.386133	0.385530
8.00	0.587123	0.598824	15.50	0.440959	0.447948	23.00	0.383858	0.384129
8.25	0.601472	0.594624	15.75	0.438600	0.444792	23.25	0.382158	0.382786
8.50	0.608745	0.588646	16.00	0.435882	0.441751	23.50	0.380843	0.381498
8.75	0.606428	0.581687	16.25	0.433357	0.438825	23.75	0.379629	0.380253
9.00	0.595098	0.574277	16.50	0.431072	0.436004	24.00	0.378328	0.379060
9.25	0.582353	0.566815	16.75	0.429321	0.433298	24.25	0.376652	0.377923
9.50	0.569721	0.559514	17.00	0.428472	0.430678	24.50	0.375159	0.376824
9.75	0.557017	0.552519	17.25	0.428513	0.428153	24.75	0.374110	0.375775
10.00	0.546297	0.545860	17.50	0.428718	0.425703	25.00	0.373398	0.374777
10.25	0.539027	0.539584	17.75	0.429228	0.423330	25.25	0.373063	0.373802
10.50	0.532312	0.533653	18.00	0.429191	0.421022	25.50	0.372972	0.372881
10.75	0.525319	0.528030	18.25	0.427666	0.418780	25.75	0.373097	0.372006
11.00	0.517219	0.522696	18.50	0.424777	0.416582	26.00	0.372843	0.371187
11.25	0.508160	0.517583	18.75	0.420150	0.414440	26.25	0.372574	0.370401
11.50	0.499614	0.512669	19.00	0.414664	0.412341	26.50	0.371913	0.369696
11.75	0.492452	0.507908	19.25	0.408856	0.410276	26.75	0.370719	0.369048
12.00	0.487600	0.503277	19.50	0.404195	0.408252	27.00	0.369429	0.368482
12.25	0.484779	0.498742	19.75	0.400397	0.406250	27.25	0.367981	0.368004
12.50	0.486303	0.494308	20.00	0.397787	0.404309	27.50	0.366724	0.367612
12.75	0.490573	0.489944	20.25	0.396463	0.402376	27.75	0.365956	0.367345
13.00	0.496593	0.485666	20.50	0.396219	0.400494	28.00	0.365744	0.367167
13.25	0.501025	0.481464	20.75	0.396236	0.398642	28.25	0.365755	0.367087
13.50	0.501481	0.477344	21.00	0.396823	0.396831	28.50	0.366065	0.367091
13.75	0.495004	0.473302	21.25	0.396477	0.395076	28.75	0.366482	0.367145
14.00	0.483556	0.469357	21.50	0.396072	0.393352	29.00	0.366532	0.367189
14.25	0.469976	0.465516	21.75	0.394739	0.391688	29.25	0.366638	0.367122
14.50	0.458267	0.461771	22.00	0.393127	0.390066	29.50	0.366687	0.366848
14.75	0.449774	0.458136	22.25	0.391069	0.388492	29.75	0.366640	0.366189
15.00	0.445379	0.454620	22.50	0.388645	0.386980			

Diffraction pattern 2

S	$I^{tot}(s)$	$I^{b}(s)$	s	$I^{tot}(s)$	$I^{b}(s)$	S	$I^{tot}(s)$	$I^{b}(s)$
7.75	0.576203	0.602580	15.25	0.442941	0.451030	22.75	0.385567	0.385050
8.00	0.588663	0.600600	15.50	0.440924	0.447796	23.00	0.383536	0.383648
8.25	0.602886	0.595984	15.75	0.438545	0.444669	23.25	0.381781	0.382299
8.50	0.609165	0.589692	16.00	0.435801	0.441636	23.50	0.380487	0.380994
8.75	0.606171	0.582447	16.25	0.433219	0.438707	23.75	0.379214	0.379748
9.00	0.596170	0.574780	16.50	0.430969	0.435877	24.00	0.377873	0.378556
9.25	0.582834	0.567067	16.75	0.429271	0.433133	24.25	0.376310	0.377400
9.50	0.569231	0.559508	17.00	0.428158	0.430483	24.50	0.374774	0.376324
9.75	0.556377	0.552248	17.25	0.428116	0.427928	24.75	0.373585	0.375285
10.00	0.545902	0.545355	17.50	0.428450	0.425430	25.00	0.372884	0.374294
10.25	0.537500	0.538841	17.75	0.428857	0.423020	25.25	0.372395	0.373360
10.50	0.531072	0.532704	18.00	0.428578	0.420687	25.50	0.372498	0.372481
10.75	0.524360	0.526916	18.25	0.427322	0.418396	25.75	0.372572	0.371663
11.00	0.516277	0.521435	18.50	0.424446	0.416178	26.00	0.372523	0.370892
11.25	0.507246	0.516221	18.75	0.419870	0.413995	26.25	0.372377	0.370194
11.50	0.498665	0.511246	19.00	0.414322	0.411873	26.50	0.371642	0.369565
11.75	0.491639	0.506453	19.25	0.408611	0.409796	26.75	0.370586	0.369003
12.00	0.486581	0.501833	19.50	0.403650	0.407752	27.00	0.369515	0.368526
12.25	0.484341	0.497341	19.75	0.399865	0.405756	27.25	0.368098	0.368132
12.50	0.484917	0.492988	20.00	0.397147	0.403798	27.50	0.367207	0.367839
12.75	0.489173	0.488719	20.25	0.396047	0.401873	27.75	0.366377	0.367626
13.00	0.494912	0.484543	20.50	0.395623	0.399999	28.00	0.366148	0.367524
13.25	0.499179	0.480462	20.75	0.395784	0.398152	28.25	0.366342	0.367504
13.50	0.499378	0.476467	21.00	0.396250	0.396352	28.50	0.366470	0.367555
13.75	0.493754	0.472559	21.25	0.396024	0.394595	28.75	0.366843	0.367657
14.00	0.482882	0.468737	21.50	0.395298	0.392882	29.00	0.367010	0.367751
14.25	0.469878	0.464995	21.75	0.394414	0.391222	29.25	0.367310	0.367795
14.50	0.458195	0.461354	22.00	0.392574	0.389600	29.50	0.367554	0.367669
14.75	0.449944	0.457814	22.25	0.390583	0.388036	29.75	0.367729	0.367253
15.00	0.445132	0.454379	22.50	0.388066	0.386527			

Table S9 Equilibrium (r_e) and thermal–average (r_g, r_a) distances, vibrational corrections (Δ), and mean amplitudes (u) for internuclear distances of the *boat* conformation of MDABH obtained for 293 K using the GED (MP2 dynamic model) refinement (in Å).
(n is the number of equivalent parameters)

Atomic pair	n	r_e	r_g	r_a	Δr	Δr(har)	Δr(kin)	Δr(dyn)	Δr(rot)	u
C6-H8	1	1.0733	1.1059	1.1003	0.0326	0.0156	-0.0118	0.0289	-0.0001	0.0788
C3-H11	1	1.0743	1.1098	1.1042	0.0355	0.0176	-0.0138	0.0317	0.0000	0.0785
C7-H15	1	1.0746	1.1083	1.1027	0.0337	0.0168	-0.0134	0.0303	0.0000	0.0788
C3-H12	1	1.0751	1.1108	1.1051	0.0357	0.0184	-0.0148	0.0320	0.0001	0.0786
C2-H9	2	1.0765	1.1122	1.1066	0.0358	0.0187	-0.0146	0.0317	0.0000	0.0791
C7-H16	2	1.0773	1.1095	1.1038	0.0322	0.0153	-0.0118	0.0288	-0.0001	0.0790
C2-H10	2	1.0775	1.1137	1.1080	0.0362	0.0191	-0.0153	0.0325	-0.0001	0.0792
N1-C6	2	1.4404	1.4514	1.4497	0.0111	0.0030	-0.0013	0.0094	0.0000	0.0497
C2-N1	2	1.4663	1.4788	1.4770	0.0125	0.0038	-0.0022	0.0109	0.0000	0.0520
C6-C7	1	1.4870	1.5009	1.4993	0.0139	0.0053	-0.0042	0.0128	0.0000	0.0496
N1-N5	1	1.5121	1.5293	1.5271	0.0172	0.0028	-0.0042	0.0187	-0.0001	0.0582
C2-C3	2	1.5233	1.5366	1.5348	0.0134	0.0041	-0.0032	0.0125	0.0000	0.0524
H11-H12	1	1.7364	1.7858	1.7771	0.0494	0.0228	-0.0200	0.0466	0.0000	0.1236
H9-H10	2	1.7501	1.7992	1.7905	0.0491	0.0244	-0.0219	0.0466	0.0000	0.1245
H16-H17	1	1.7518	1.7962	1.7874	0.0445	0.0177	-0.0189	0.0456	0.0001	0.1254
H15-H16	2	1.7538	1.7980	1.7893	0.0442	0.0175	-0.0188	0.0455	0.0000	0.1250
N1-H9	2	2.0332	2.0665	2.0611	0.0333	0.0130	-0.0153	0.0356	0.0000	0.1054
N1-H10	2	2.0599	2.0934	2.0878	0.0335	0.0124	-0.0145	0.0356	0.0000	0.1078
C6-H15	1	2.0963	2.1332	2.1277	0.0369	0.0138	-0.0168	0.0400	-0.0001	0.1086
C6-H16	2	2.1192	2.1504	2.1450	0.0312	0.0109	-0.0131	0.0334	0.0000	0.1081
N1-H8	2	2.1602	2.1936	2.1888	0.0334	0.0089	-0.0128	0.0373	0.0000	0.1022
C3-H9	2	2.1627	2.1976	2.1924	0.0348	0.0122	-0.0138	0.0365	-0.0001	0.1063
H8-H11	1	2.1683	2.2053	2.1846	0.0370	0.0156	-0.0125	0.0338	0.0001	0.1629
C2-H11	2	2.1714	2.2032	2.1980	0.0318	0.0115	-0.0133	0.0337	-0.0001	0.1069
C2-H12	2	2.1744	2.2107	2.2054	0.0363	0.0124	-0.0153	0.0392	0.0000	0.1083
C3-H10	2	2.1921	2.2261	2.2210	0.0340	0.0127	-0.0136	0.0348	0.0001	0.1070
C7-H8	1	2.1962	2.2248	2.2201	0.0286	0.0108	-0.0118	0.0296	0.0000	0.1017
C2-C4	1	2.3259	2.3426	2.3409	0.0168	0.0020	-0.0072	0.0219	0.0001	0.0588
C2-N5	2	2.3805	2.3997	2.3982	0.0192	0.0021	-0.0057	0.0228	0.0000	0.0596
H9-H12	2	2.3835	2.4310	2.4189	0.0475	0.0182	-0.0153	0.0447	-0.0001	0.1709
C2-C6	2	2.4069	2.4263	2.4246	0.0194	0.0022	-0.0032	0.0204	0.0000	0.0652
H10-H11	2	2.4140	2.4544	2.4419	0.0404	0.0177	-0.0128	0.0356	-0.0001	0.1721
C3-N1	2	2.4518	2.4705	2.4691	0.0187	0.0028	-0.0047	0.0207	-0.0001	0.0577
N1-C7	2	2.4671	2.4827	2.4806	0.0155	0.0033	-0.0028	0.0150	0.0000	0.0701
C3-H8	1	2.4785	2.5173	2.5084	0.0388	0.0079	-0.0122	0.0431	0.0000	0.1294
C2-H8	2	2.5317	2.5680	2.5601	0.0363	0.0066	-0.0105	0.0402	0.0000	0.1426
H8-H16	2	2.5525	2.5884	2.5775	0.0359	0.0139	-0.0158	0.0377	0.0001	0.1659
N1-H15	2	2.5534	2.5832	2.5738	0.0298	0.0100	-0.0106	0.0304	0.0000	0.1532
H8-H10	2	2.6888	2.7317	2.7126	0.0428	0.0100	-0.0101	0.0429	0.0000	0.2226
C3-C6	1	2.7332	2.7572	2.7551	0.0240	0.0027	-0.0067	0.0280	0.0000	0.0595
H10-H12	2	2.7731	2.8220	2.8135	0.0489	0.0182	-0.0238	0.0545	0.0000	0.1520
C6-H10	2	2.7852	2.8206	2.8126	0.0355	0.0073	-0.0105	0.0387	0.0000	0.1476
C2-H13	2	2.8173	2.8515	2.8432	0.0341	0.0071	-0.0219	0.0489	0.0000	0.1317
C6-H11	1	2.8292	2.8597	2.8497	0.0305	0.0072	-0.0162	0.0395	0.0000	0.1334
H9-H13	1	2.9144	2.9552	2.9326	0.0407	0.0096	-0.0305	0.0616	0.0000	0.2010
N1-H13	2	2.9224	2.9593	2.9529	0.0369	0.0075	-0.0206	0.0500	0.0000	0.1320
N1-H16	2	2.9271	2.9549	2.9491	0.0278	0.0075	-0.0096	0.0299	0.0000	0.1296
N1-H11	2	2.9862	3.0172	3.0113	0.0310	0.0074	-0.0168	0.0404	0.0000	0.1260
H9-H11	2	3.0240	3.0768	3.0714	0.0528	0.0155	-0.0249	0.0622	0.0000	0.1280
H8-H15	1	3.0476	3.0997	3.0947	0.0521	0.0152	-0.0272	0.0642	-0.0001	0.1249
N1-H14	2	3.2222	3.2621	3.2586	0.0400	0.0071	-0.0180	0.0508	0.0001	0.1070
C2-H14	2	3.2565	3.2939	3.2908	0.0374	0.0070	-0.0187	0.0492	-0.0001	0.1009
C6-H9	2	3.2793	3.3179	3.3148	0.0387	0.0076	-0.0183	0.0493	0.0001	0.1016

N1-H12	2	3.3324	3.3739	3.3707	0.0414	0.0080	-0.0175	0.0510	-0.0001	0.1027
N1-H17	2	3.3491	3.3835	3.3802	0.0344	0.0068	-0.0138	0.0413	0.0001	0.1046
H8-H12	1	3.5388	3.5968	3.5888	0.0580	0.0113	-0.0264	0.0732	-0.0001	0.1468
H8-H9	2	3.5674	3.6243	3.6178	0.0569	0.0099	-0.0270	0.0739	0.0001	0.1532
C2-C7	2	3.7253	3.7507	3.7492	0.0253	0.0017	-0.0061	0.0297	0.0000	0.0734
C6-H12	1	3.7921	3.8386	3.8358	0.0464	0.0074	-0.0212	0.0602	0.0000	0.0951
H9-H14	2	3.8596	3.9132	3.9067	0.0536	0.0096	-0.0357	0.0797	0.0000	0.1471
C7-H10	2	3.9536	3.9925	3.9860	0.0389	0.0050	-0.0118	0.0457	0.0000	0.1598
H10-H16	2	3.9861	4.0273	4.0154	0.0413	0.0065	-0.0110	0.0458	0.0000	0.2178
C2-H15	2	3.9913	4.0274	4.0216	0.0361	0.0054	-0.0142	0.0449	0.0000	0.1510
C2-H16	2	4.0429	4.0780	4.0728	0.0350	0.0040	-0.0114	0.0424	0.0000	0.1452
H10-H14	1	4.0603	4.1125	4.1066	0.0523	0.0087	-0.0257	0.0693	0.0000	0.1449
C3-C7	1	4.2195	4.2507	4.2492	0.0312	0.0015	-0.0108	0.0405	0.0000	0.0653
C7-H11	1	4.2573	4.2938	4.2862	0.0365	0.0042	-0.0203	0.0526	0.0000	0.1316
H10-H15	2	4.3507	4.4028	4.3939	0.0521	0.0086	-0.0233	0.0669	-0.0001	0.1969
C7-H9	2	4.4886	4.5278	4.5248	0.0393	0.0053	-0.0187	0.0526	0.0001	0.1159
C2-H17	2	4.5188	4.5607	4.5577	0.0419	0.0044	-0.0164	0.0539	0.0000	0.1161
H9-H15	2	4.5384	4.5814	4.5729	0.0430	0.0077	-0.0225	0.0577	0.0001	0.1932
H11-H16	2	4.6300	4.6751	4.6638	0.0451	0.0056	-0.0260	0.0654	0.0001	0.1788
C3-H15	1	4.6541	4.6968	4.6926	0.0428	0.0047	-0.0192	0.0572	0.0001	0.1403
C3-H16	2	4.7166	4.7599	4.7553	0.0433	0.0034	-0.0188	0.0587	0.0000	0.1349
H10-H17	2	4.7960	4.8511	4.8442	0.0551	0.0070	-0.0219	0.0700	0.0000	0.1814
H9-H16	2	4.8343	4.8822	4.8766	0.0479	0.0070	-0.0225	0.0633	0.0001	0.1640
H11-H15	1	4.9104	4.9635	4.9558	0.0531	0.0075	-0.0325	0.0781	0.0000	0.1757
C7-H12	1	5.2742	5.3261	5.3240	0.0519	0.0047	-0.0248	0.0720	0.0000	0.0995
H9-H17	2	5.3363	5.3930	5.3894	0.0567	0.0073	-0.0305	0.0800	-0.0001	0.1407
H12-H15	1	5.6452	5.7061	5.7014	0.0610	0.0066	-0.0313	0.0857	0.0000	0.1628
H12-H16	2	5.7710	5.8339	5.8292	0.0628	0.0059	-0.0329	0.0899	-0.0001	0.1557

Table S10 Correlation matrices for GED refinement of the geometrical parameters combined in independent groups.

1. Dynamic model of GED using MP2/aug-cc-pVTZ calculations

	CN, CC, NN	CH	NNC in the 5-membered ring	NC6H and $C_{Me}C6H$
CN, CC, NN	1.0000			
CH	-0.1580	1.0000		
NNC in the 5-membered ring	-0.1867	0.1278	1.0000	
NC6H and $C_{Me}C6H$	0.6270	-0.2992	-0.4442	1.0000

2. Static model of GED using MP2/aug-cc-pVTZ calculations

	CN, CC, NN	CH	NNC in the 5-membered ring	NC6H and $C_{Me}C6H$
CN, CC, NN	1.0000			
CH	-0.1530	1.0000		
NNC in the 5-membered ring	-0.1810	0.1292	1.0000	
NC6H and $C_{Me}C6H$	0.6170	-0.2976	-0.4460	1.0000

3. Static model of GED using B3LYP/aug-cc-pVTZ calculations

	CN, CC, NN	CH	NNC in the 5-membered ring	NC6H and $C_{Me}C6H$
CN, CC, NN	1.0000			
CH	-0.1403	1.0000		
NNC in the 5-membered ring	-0.1914	0.1392	1.0000	
NC6H and $C_{Me}C6H$	0.7635	-0.330	-0.5851	1.0000

Table S11. Cartesian coordinates for the MDABH molecule obtained by GED (MP2 dynamic model) refinement.

Atom	X	Y	Z
N1	1.437026	-0.756032	1.124872
C2	0.029083	-1.162935	1.078985
C3	-0.839116	0.000000	0.616265
C4	0.029083	1.162935	1.078985
N5	1.437026	0.756032	1.124872
C6	1.813676	0.000000	-0.041817
C7	3.269750	0.000000	-0.343565
H8	1.139262	0.000000	-0.876721
H9	-0.211721	-1.457222	2.086038
H10	-0.030592	-2.030127	0.442317
H11	-0.986224	0.000000	-0.447945
H12	-1.808235	0.000000	1.081609
H13	-0.211721	1.457222	2.086038
H14	-0.030592	2.030127	0.442317
H15	3.814820	0.000000	0.582552
H16	3.536530	-0.875880	-0.911192
H17	3.536530	0.875880	-0.911192

Table S12. Cartesian coordinates for the MDABH molecule obtained by GED (MP2 static model) refinement.

Atom	X	Y	Z
N1	1.436822	-0.756165	1.125527
C2	0.028794	-1.163654	1.078972
C3	-0.838701	0.000000	0.615867
C4	0.028794	1.163654	1.078972
N5	1.436822	0.756165	1.125527
C6	1.814092	0.000000	-0.041203
C7	3.270059	0.000000	-0.344766
H8	1.139829	0.000000	-0.875135
H9	-0.212991	-1.457799	2.084922
H10	-0.031100	-2.029900	0.442476
H11	-0.984966	0.000000	-0.447599
H12	-1.807371	0.000000	1.080181
H13	-0.212991	1.457799	2.084922
H14	-0.031100	2.029900	0.442476
H15	3.815817	0.000000	0.579957
H16	3.535942	-0.875188	-0.912267
H17	3.535942	0.875188	-0.912267

Table S13. Cartesian coordinates for the MDABH molecule obtained by GED (B3LYP) refinement.

Atom	X	Y	Z
N1	1.417477	-0.754784	0.959515
C2	0.010019	-1.171072	0.986002
C3	-0.918133	0.000000	0.659901
C4	0.010019	1.171072	0.986002
N5	1.417477	0.754784	0.959515
C6	1.756974	0.000000	-0.216823
C7	3.219428	0.000000	-0.518434
H8	1.077461	0.000000	-1.062676
H9	-0.147191	-1.540272	1.996120
H10	-0.086934	-2.012277	0.303636
H11	-1.229337	-0.000000	-0.379844
H12	-1.820018	0.000000	1.263581
H13	-0.147191	1.540272	1.996120
H14	-0.086934	2.012277	0.303636
H15	3.785122	0.000000	0.406955
H16	3.490504	-0.881723	-1.096047
H17	3.490504	0.881723	-1.096047