Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 474–477

Molecular structure of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane: gas phase electron diffraction and theoretical study

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Experimental Section

Synthesis: A sample of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6** was synthesized at the N. D. Zelinsky Institute of Organic Chemistry, RAS, and used without further purification.
IR spectrum: The IR spectrum of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6** was recorded on Bruker "Alpha" spectrometers in the range of 400-4000 cm^{-1} with resolution of 2 cm^{-1}.
Mass spectrum: Mass spectra were measured using a Finnigan MAT INCOS-50 instrument. High resolution mass spectra were recorded on a Bruker microTOF spectrometer with electrospray ionization.
NMR Experiments: All the NMR spectra were recorded at 293 K on Bruker AV-400 instrument equipped with a Z-gradient broadband observe probe.
Gas-Phase Electron Diffraction Experiment: The GED experiment was carried out at the Moscow State University on the EG-100 M apparatus.

Synthesis: A solution of Bu^tOCl (2.2 ml, 16.5 mmol) in MeOH (3 ml) was added dropwise to a magnetically stirred solution of 1,3-diaminopropane (2.4 g, 33 mmol) in MeOH (15 ml) at –5-0 ºC. Cyclopropanecarbaldehyde (1.2 g, 16.6mmol) was then added. The reaction mixture was stirred at 0–5 ºC for 24 h. The solid formed was filtered off, the solvent was evaporated under reduced pressure, and $CHCl_3$ (60 ml) was added to the residue. The precipitate was filtered off, the solution was washed with water (50 ml), dried with K_2CO_3 and the solvent was evaporated *in vacuo*. The resulting residue was distilled at reduced pressure to yield a light liquid. Bp: 110−111 °C (25 Torr). Yield 1.4 g (68%). d_4^{20} 1.02 g cm^{-3}, n_D^{20} 1.490.

The IR spectrum of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane was recorded on Bruker "Alpha" spectrometers in the range 400-4000 cm^{-1} (resolution 2 cm^{-1}), ν = 641, 696, 778, 814, 846, 880, 911, 953, 969, 990, 1025, 1053, 1088, 1143, 1188, 1220, 1251, 1291, 1423, 1449, 1477, 1650, 2879, 2944, 2982, 3084, 3414 $cm^{–1}$.

Mass spectrum: All measurements were performed in a positive (+MS) ion mode (interface capillary voltage: 4500 V) with scan range *m/z*: 50-3000.
HRMS (ESI): *m/z* for $C_7H_{12}N_2(M+H)^+$:calcd. 125.1073, found 125.1076.

Mass-spectra (EI, 70 eV), *m/z* (%): 124 (6) $[M]^+$, 123 (20) $[M − H]^+$, 109 (21) $[M – H – (-CH_2-)]^+$, 96 (31) $[M − (-CH_2-CH_2-)]^+$, 81 (24)$[M– H–{}^{cyclo}Pr]^+$, 68(65)$[M –{}^{cyclo}Pr– (-CH_2-)]^+$, 54 (19) $[M –{}^{cyclo}Pr– (-CH_2-CH_2-)]^+$, 41(100) $[{}^{cyclo}Pr– H]^+$, 28 (100) $[N_2]^+$.

NMR Experiments: A 25-mg portion of the sample was dissolved in $CDCl_3$ (0.6 ml) The ^1H and ^{13}C chemical shifts (δ), for which values are reported in ppm, were calibrated against the residual protons (7.27 ppm) and carbon atoms (77.00 ppm) of the solvent. The coupling constants, *J*, are given in Hz. Multiplicities are indicated by s (singlet),d (doublet), t (triplet) and m (multiplet).

An analysis of the ^{1}H and ^{13}C 1D NMR spectra of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6** (Figures S1, S2) showed that in solution the compound existed only in a single conformation (i.e., there were clean peaks of only one compound).

^{1}H NMR (400.16 MHz, $CDCl_3$) δ, ppm, *J*/Hz: 0.25 – 0.33 (m, 2H, ^{cyclo}Pr,H-20,18), 0.33 – 0.42 (m, 2H, ^{cyclo}Pr, H-21,19), 0.76 – 0.85 (m, 1H, ^{cyclo}Pr, H-17), 1.58–1.77 (m, 2 H, CH_2, H-13,12),2.09 – 2.11 (d, 1H, HC_{ring}, H-16), 2.84 – 2.93 (dt, 2 H, 2×N–CH_{ax}, H-10,14), 3.21–3.28 (dt, 2 H, 2×N–CH_{eq}, H-11,15). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ, ppm.: 1.24 (2×CH_2, ^{cyclo}Pr, C-9,8), 10.79 (CH, ^{cyclo}Pr, C-7), 21.81 (CH_2, C-3), 51.28 (2×N-CH_2, C-2,4), 57.92 (HC_{ring}, C-6).

For further approval, set of 2D spectra {^{1}H-^{13}C}HSQC (*Heteronuclear Spectroscopy Quantum Correlation*), {^{1}H-^{13}C}HMBC (*Heteronuclear Multiple Bond Correlation*) and {^{1}H-^{1}H}gNOESY (*Nuclear Overhauser Effect Spectroscopy*), was measured in the $CDCl_3$ solution at 298 K (Figures S3-S5), that makes it possible to assign all the protons and carbon atoms and relations between them. The mixing time in NOESY was 0.7 s. All correlation NMR spectra were acquired with standard Bruker parameters.

The data of the heteronuclear correlation NMR spectra {^{1}H-^{13}C}HSQC and {^{1}H-^{13}C}HMBC are presented in Table S1. These spectra show how far away each proton is found from a particular carbon atom: respectively, through one or 2-3 bonds. The 2D NMR spectrum {^{1}H-^{1}H}gNOESY shows the spatial arrangement of the protons relative to each other (Table S2 and Fig. S5). Proton H16 has cross-peaks with protons H20 (Fig. S6) and H12 (Fig. S7). The mixing time in the NOESY spectrum was 0.7 s.

The 2D NMR spectrum {^{1}H-^{1}H}gNOESY showed that the proton H16 has cross-peaks with protons H18 (Figure S7), indicating existence in solution the *gauche-boat* conformation, since such an interaction is not specific for the *anti-boat* conformation.

Gas-Phase Electron Diffraction Experiment: The details of the experimental conditions are given in Table S3. The electron wavelength was calibrated with CCl_4 scattering patterns. The optical densities were measured using a commercial Epson Perfection 4870 photo scanner. The numerical values of the experimental intensity curves *I*(s) with the backgrounds are available in Table S4. The final modified intensity curve is shown in Figure S8.

Table S1. The {^{1}H-^{13}C}HSQC and {^{1}H-^{13}C}HMBC data for 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6**. Atom numeration is given in Figure 2 of the main text.

Atoms numbers	^{13}C NMR, chemical shift, ppm	^{1}H-^{13}C HSQC interactions	^{1}H-^{13}C HMBC interactions
C-9	1.24	H-20,21	H-16,17,19,18
C-8	1.24	H-19,18	H-16,17,20,21
C-7	10.76	H-17	H-16,20,1,19,18
C-6	57.92	H-16	H-10,11,14,15,20,21,19,18
C-2	51.28	H-10,11	H-15,16,12,13
C-4	51.28	H-14,15	H-11,16,12,13

Table S2 The {^{1}H-^{1}H}gNOESY data of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6**. Atom numeration is given in Figure 2 of the main text.

Atoms number	^{1}H NMR chemical shift, ppm	Coupling constant, (*J* Hz)	^{1}H-^{1}HgNOESY interations
H-20	0.25-0.33, m, 1H	-	H-16,17,21,19,18
H-18	0.25-0.33, m, 1H	-	H-17,21,19,18
H-21	0.33-0.42, m, 1H	-	H-17,20,19,18
H-19	0.33-0.42, m, 1H	-	H-17,20,21,18
H-17	0.76-0.85, m, 1H	-	H-16,21,19
H-12	1.55-1.65, m, 1H	-	H-10,14,16,13
H-13	1.65-1.76, m, 1H	-	H-11,15,13
H-16	2.09-2.11, d, 1H	4.7 ($^{3}J_{H14-H15}$)	H-20,12
H-10	2.84-2.92, dt, 1H	-11.8 ($^{2}J_{H10-H11}$) 11.3 ($^{3}J_{H10-H21}$) 8.2 ($^{3}J_{H10-H20}$)	H-11,12
H-14	2.84-2.93, dt, 1H	-11.8 ($^{2}J_{H12-H13}$) 11.3 ($^{3}J_{H12-H21}$) 8.2 ($^{3}J_{H13-H20}$)	H-15,12
H-11	3.21-3.28, dt, 1H	-11.8 ($^{2}J_{H11-H10}$) 8.5 ($^{3}J_{H11-H21}$) 2.0 ($^{3}J_{H11-H20}$)	H-10,13
H-15	3.21-3.28, dt, 1H	-11.8 ($^{2}J_{H13-H12}$) 8.5 ($^{3}J_{H13-H21}$) 2.0 ($^{3}J_{H13-H20}$)	H-14,13

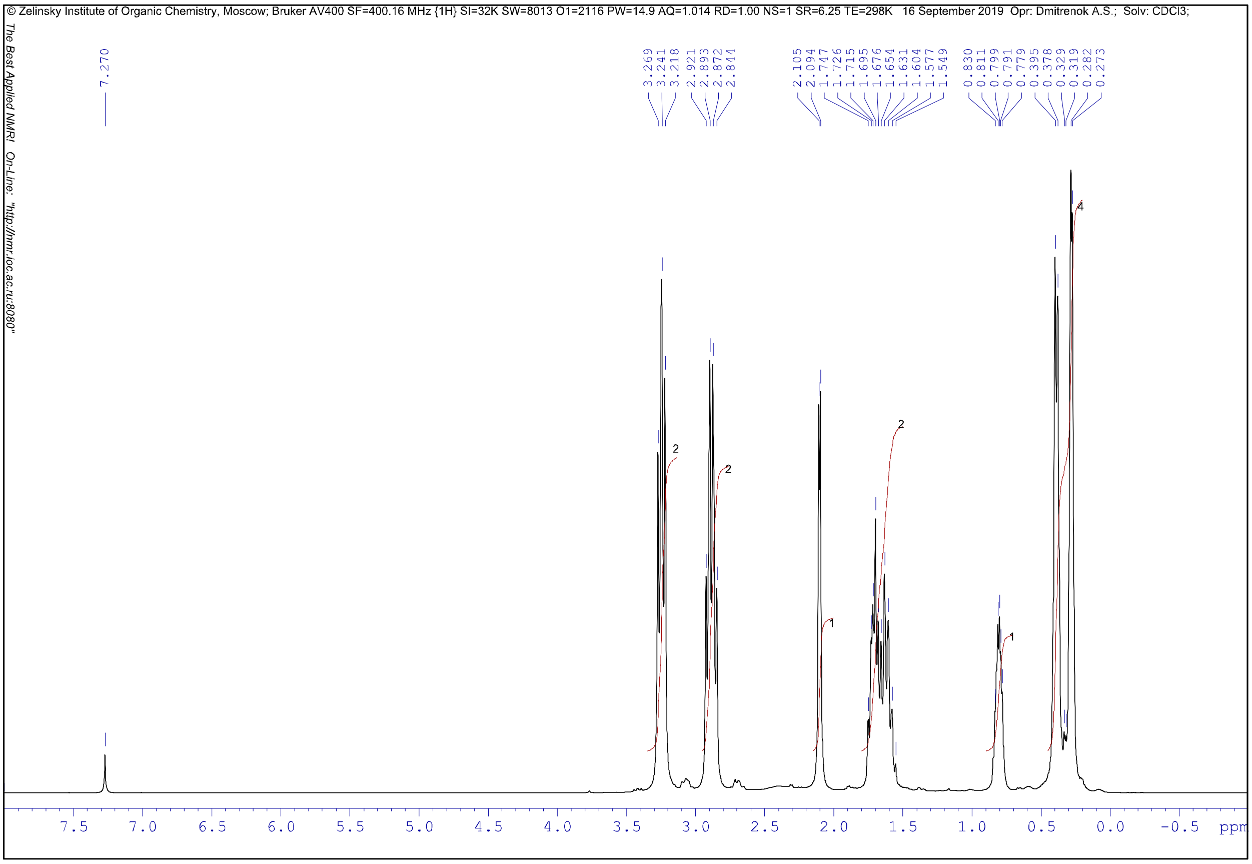

Figure S1. [1]H NMR spectrum of *6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane* (solution in $CDCl_3$).

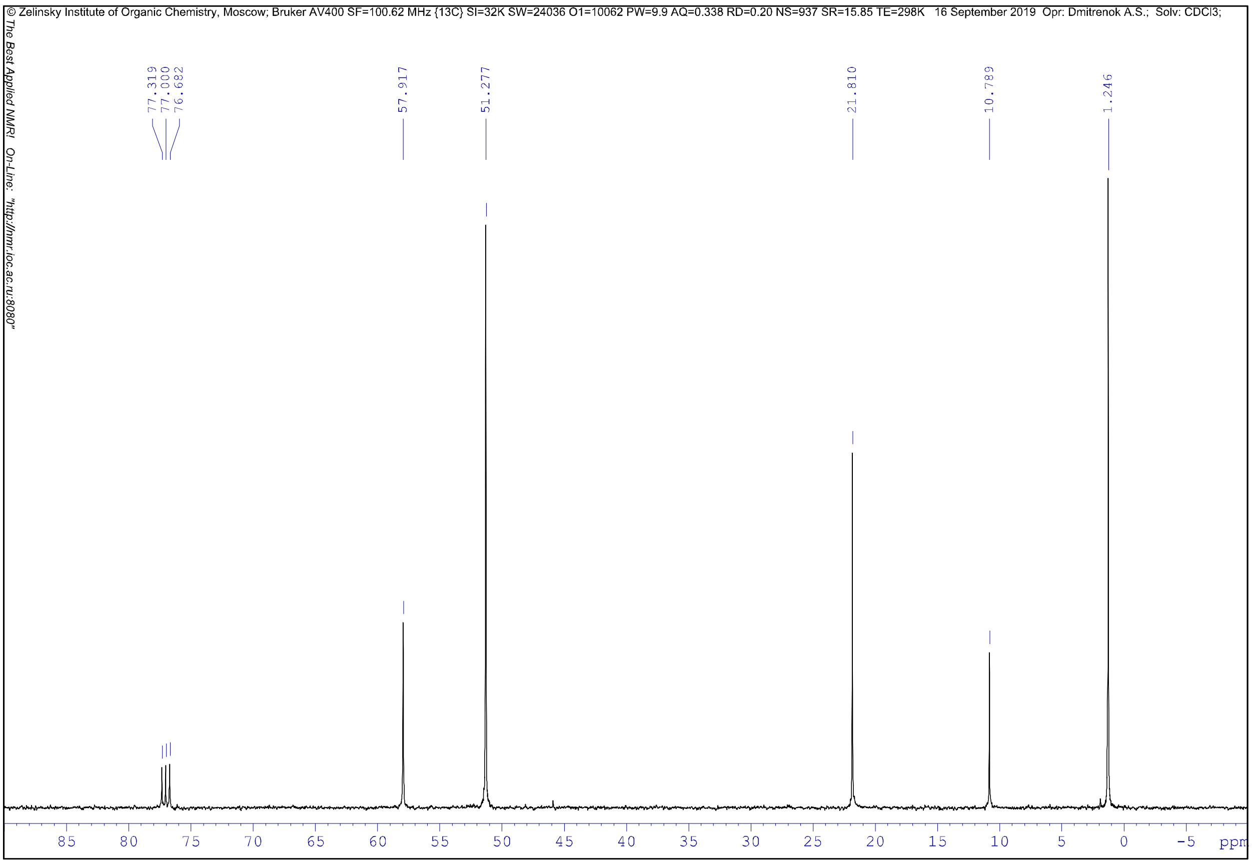

Figure S2. [13]C NMR spectrum of *6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane* (solution in $CDCl_3$).

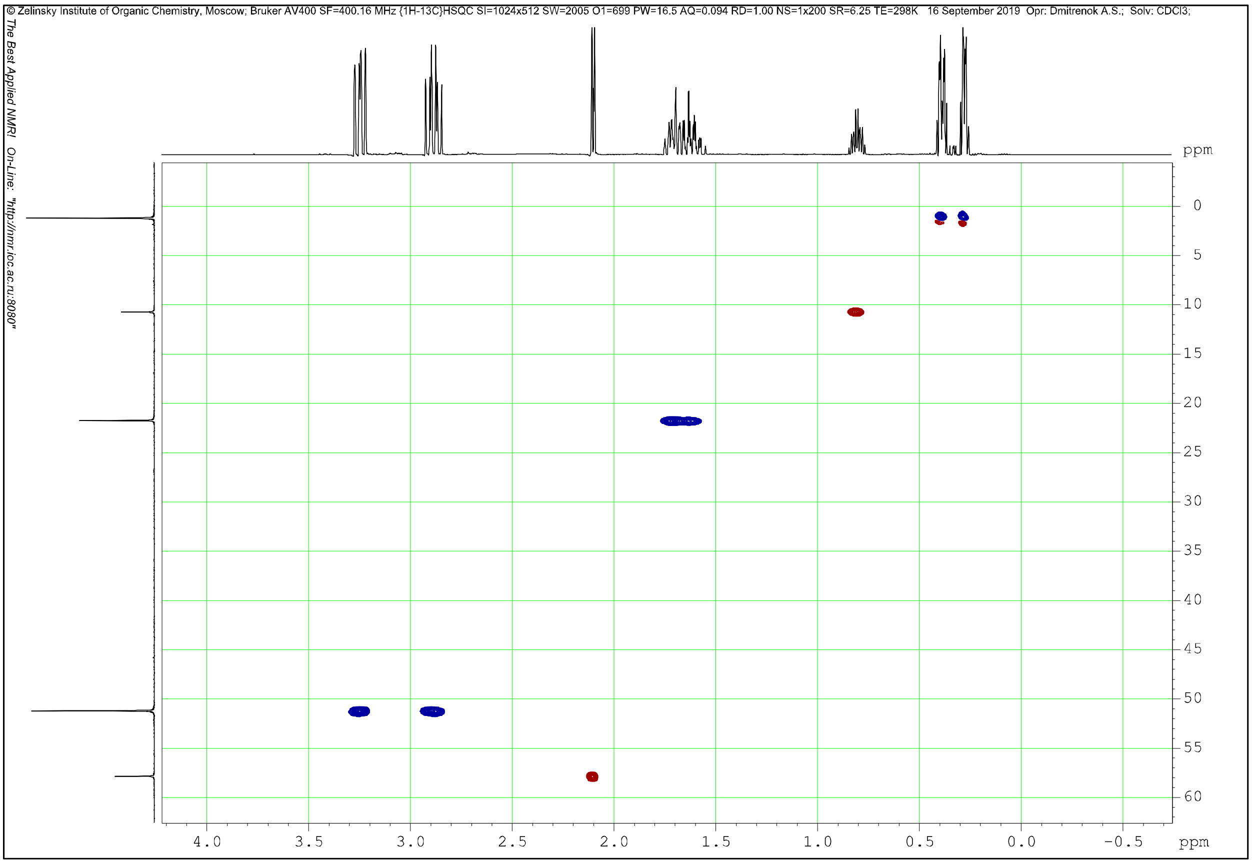

Figure S3. {^{1}H-^{13}C}HSQC spectrum of *6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane* (solution in $CDCl_3$).

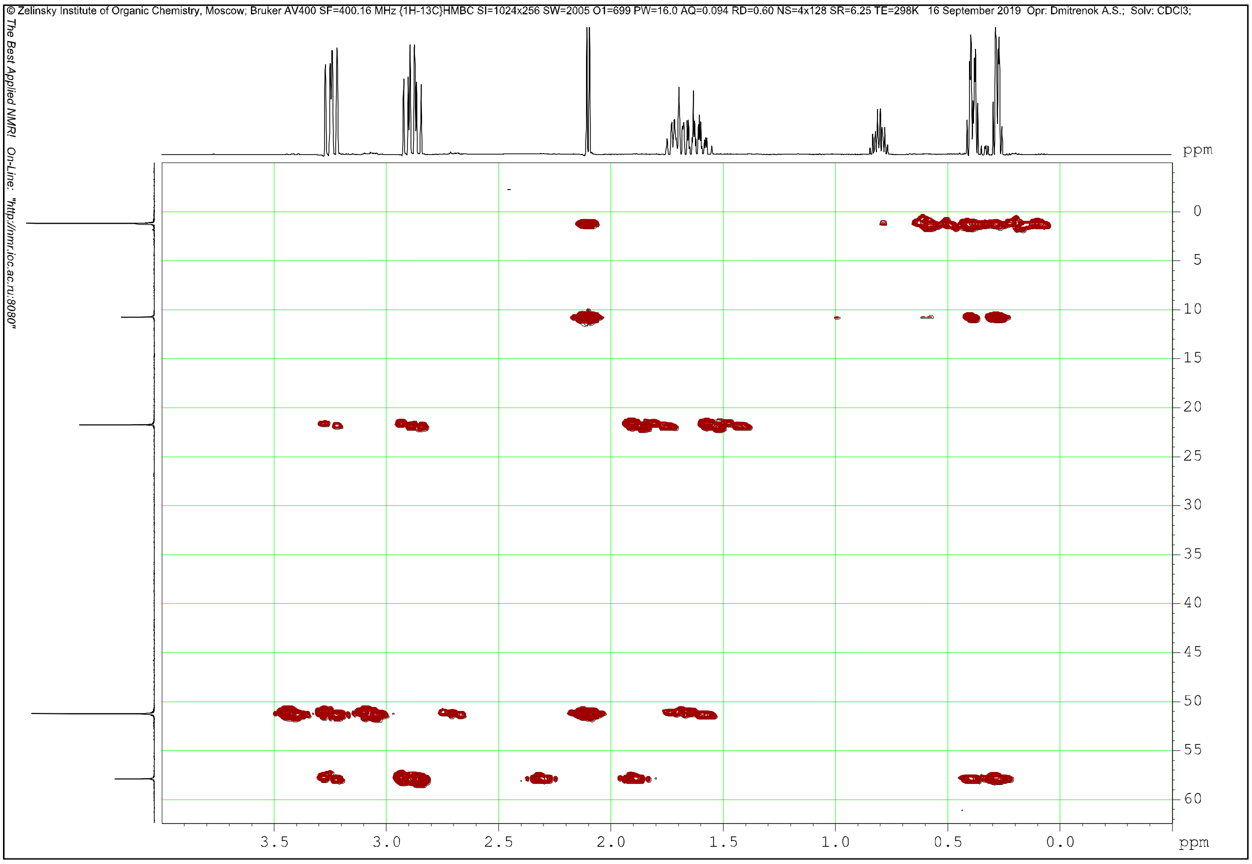

Figure S4. {^{1}H-^{13}C}HMBC spectrum of *6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane* (solution in $CDCl_3$).

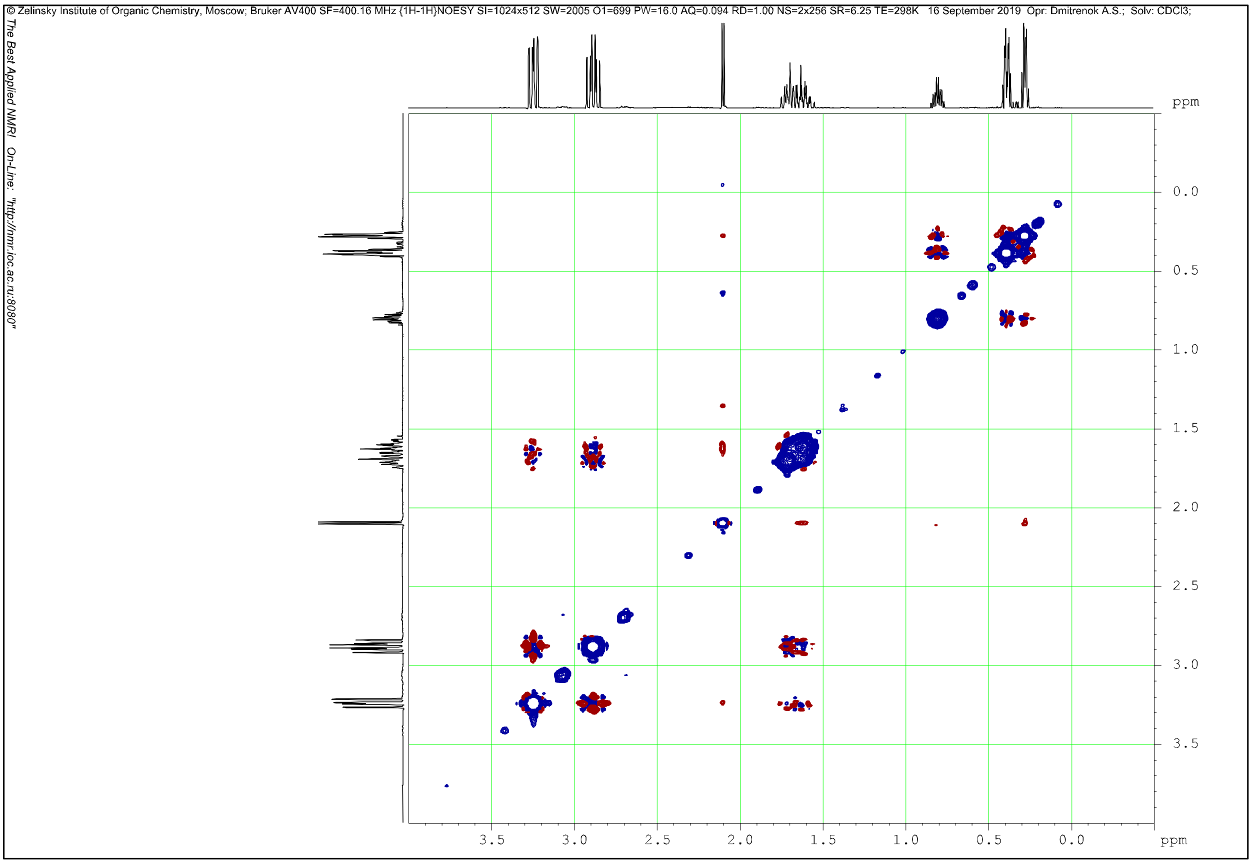

Figure S5. {1H–1H}gNOESY spectrum of *6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane* (solution in $CDCl_3$).

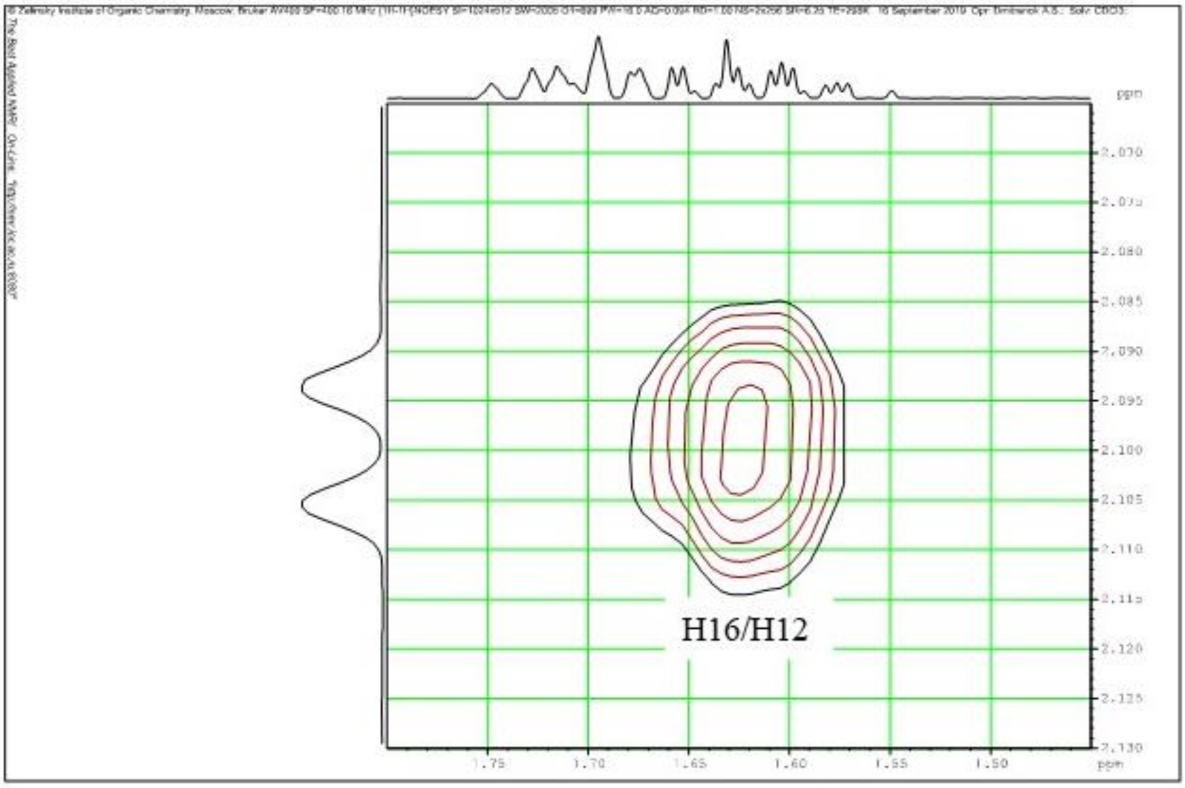

Figure S6. Fragment of the {1H–1H}gNOESY spectrum for the of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane. (see Fig. S4). The NMR spectra of protons are shown on the axes. Atom numeration is given in Fig. 2.

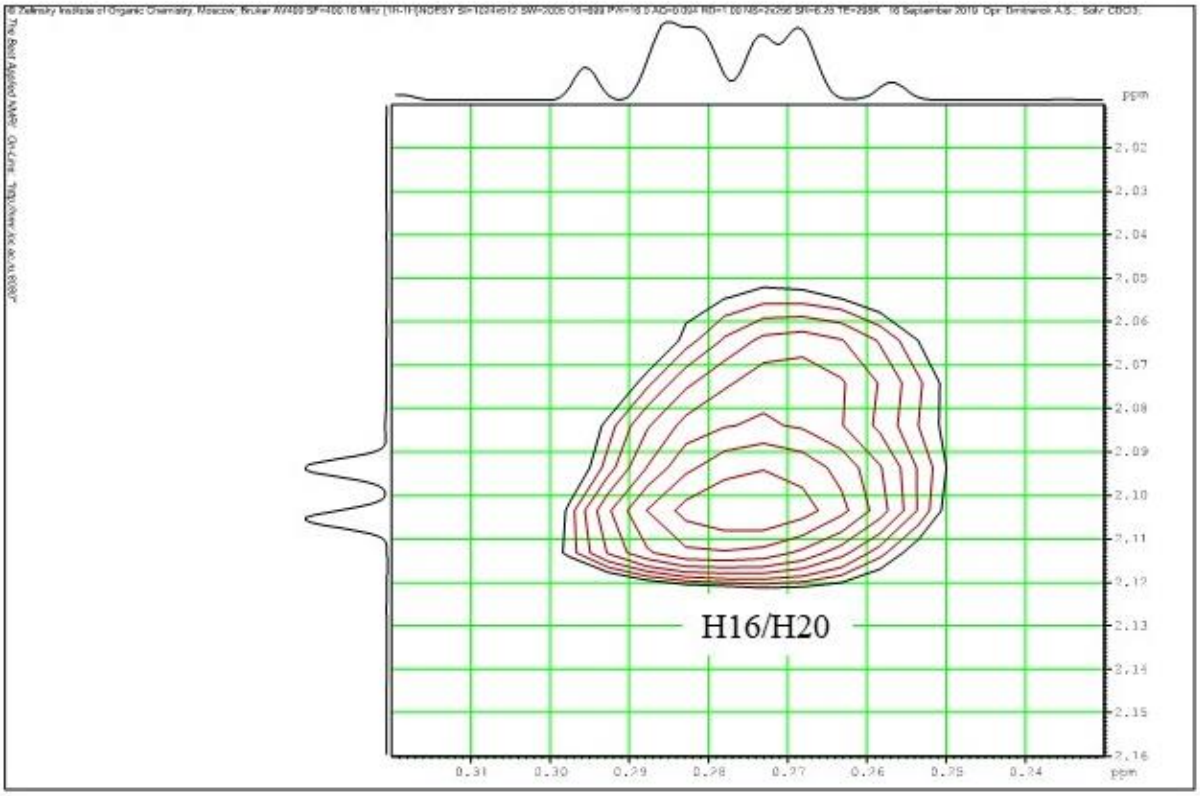

Figure S7. Fragment of the {1H–1H}gNOESY spectrum for the of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane. (see Fig. S4). The NMR spectra of protons are shown on the axes. Atom numeration is given in Fig. 2.

Table S3. Conditions of the GED experiment for 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6**

Nozzle-to-film distance, mm	362.3 (LD)	193.9 (SD)
Beam current, µA	2.0	2.0
Exposure time, sec	35, 40, 35	45, 45, 45
Nozzle temperature, K	315	320
Residual gas pressure, mm Hg	$3.0 \cdot 10^{-5}$	$3.0 \cdot 10^{-5}$
Number of the diffraction patterns (substance)	3	3
Number of the diffraction patterns (standard CCl_4)	2	2
Wavelength of electrons (λ), Å	0.04976	0.050217
Interval of scattering variable (s^a), $Å^{-1}$	3.4 – 17.0 (Δs = 0.2)	6.6 – 27.4 (Δs = 0.2)

$^a s=4\pi\lambda^{-1}\sin(\theta/2)$, where θ is the scattering angle, λ is the electron wavelength.

Table S4. Experimental total intensity curves *I*(*s*) and background lines *B*(*s*).

a) Long nozzle-to-film distance *L* = 362.2 mm

s [$Å^{-1}$]	*I*(*s*)	*B*(*s*)
3.40	0.392758240	0.433360862
3.60	0.397954140	0.444127501
3.80	0.402302870	0.454643762
4.00	0.408118230	0.464687553
4.20	0.420954460	0.474040365
4.40	0.438604260	0.482386665
4.60	0.463686680	0.489362256

4.80	0.494160070	0.494597623
5.00	0.528917460	0.497746751
5.20	0.555702760	0.498499508
5.40	0.568379990	0.496717667
5.60	0.566406400	0.492504251
5.80	0.552226670	0.486189672
6.00	0.530442500	0.478289180
6.20	0.503257490	0.469423569
6.40	0.472387200	0.460231704
6.60	0.440125120	0.451291991
6.80	0.412746190	0.443065020
7.00	0.393205630	0.435842551
7.20	0.384020000	0.429745694
7.40	0.383335200	0.424713844
7.60	0.387584580	0.420531691
7.80	0.394639110	0.416906173
8.00	0.403093540	0.413556369
8.20	0.411873690	0.410292264
8.40	0.419493130	0.407043857
8.60	0.424163230	0.403831043
8.80	0.424273490	0.400710555
9.00	0.419749720	0.397745722
9.20	0.412966660	0.395001253
9.40	0.405880160	0.392544746
9.60	0.400448760	0.390458708
9.80	0.396886780	0.388836077
10.00	0.394703280	0.387760822
10.20	0.392610810	0.387277819
10.40	0.389711330	0.387375001
10.60	0.385819640	0.387984400
10.80	0.381199260	0.389000290
11.00	0.377117090	0.390302718
11.20	0.374301840	0.391767978
11.40	0.373171810	0.393279689
11.60	0.374026100	0.394740702
11.80	0.376612830	0.396081808
12.00	0.381328590	0.397266395
12.20	0.387245710	0.398283909
12.40	0.394107620	0.399156252
12.60	0.401635660	0.399938882
12.80	0.408900670	0.400726213
13.00	0.416108950	0.401662768
13.20	0.422235790	0.402930794
13.40	0.426956890	0.404729381
13.60	0.429490530	0.407234852
13.80	0.430310420	0.410561184
14.00	0.429507480	0.414727751
14.20	0.428743020	0.419658095
14.40	0.428128050	0.425199622
14.60	0.428610680	0.431176485

14.80	0.430906970	0.437424897
15.00	0.434585620	0.443804709
15.20	0.439211230	0.450208057
15.40	0.444072860	0.456561398
15.60	0.449297070	0.462822178
15.80	0.455310500	0.468963663
16.00	0.461951310	0.474966604
16.20	0.469203670	0.480831384
16.40	0.477251940	0.486585224
16.60	0.485606660	0.492272072
16.80	0.494391970	0.497936982
17.00	0.503703540	0.503603646

b) Nozzle-to-film distance L = 193.9 mm

s [Å^{-1}]	$I(s)$	$B(s)$
6.60	0.227299630	0.233316533
6.80	0.225216580	0.232746801
7.00	0.221279800	0.231981040
7.20	0.217228530	0.230911521
7.40	0.216650490	0.229550730
7.60	0.215987070	0.227955841
7.80	0.218347060	0.226180145
8.00	0.221091450	0.224215740
8.20	0.222895890	0.222034237
8.40	0.224010090	0.219643083
8.60	0.223051650	0.217093126
8.80	0.221051650	0.214458023
9.00	0.218434020	0.211784647
9.20	0.214986690	0.209073143
9.40	0.210997600	0.206304192
9.60	0.207366770	0.203475184
9.80	0.203327150	0.200619569
10.00	0.199746480	0.197810898
10.20	0.196291680	0.195130637
10.40	0.193012270	0.192637901
10.60	0.189439310	0.190355274
10.80	0.185946330	0.188275544
11.00	0.182670230	0.186371682
11.20	0.179789960	0.184609551
11.40	0.177447940	0.182958334
11.60	0.175641930	0.181395532
11.80	0.174586170	0.179906394
12.00	0.174080230	0.178478369
12.20	0.173919800	0.177098677
12.40	0.174276850	0.175751065
12.60	0.174661690	0.174411064
12.80	0.175402030	0.173050126
13.00	0.175628460	0.171642161
13.20	0.175274500	0.170180447
13.40	0.174260830	0.168680176

13.60	0.172614270	0.167166696
13.80	0.170516630	0.165659442
14.00	0.167896910	0.164163004
14.20	0.165013190	0.162672451
14.40	0.161959960	0.161184034
14.60	0.159237200	0.159704432
14.80	0.156899830	0.158251028
15.00	0.154639290	0.156851113
15.20	0.152875630	0.155537375
15.40	0.151672300	0.154331864
15.60	0.150429470	0.153238911
15.80	0.149534130	0.152252559
16.00	0.148843660	0.151358912
16.20	0.148446870	0.150541036
16.40	0.148004770	0.149783443
16.60	0.147776730	0.149074752
16.80	0.147902340	0.148400374
17.00	0.147710750	0.147739281
17.20	0.147713470	0.147071368
17.40	0.147552780	0.146376877
17.60	0.147481820	0.145640771
17.80	0.147098330	0.144855904
18.00	0.146437900	0.144029395
18.20	0.145536660	0.143181144
18.40	0.144395110	0.142336138
18.60	0.143164640	0.141515862
18.80	0.141954020	0.140732029
19.00	0.140294050	0.139988575
19.20	0.138851360	0.139288906
19.40	0.137701960	0.138630763
19.60	0.136462150	0.138006969
19.80	0.135530900	0.137412838
20.00	0.134926210	0.136844029
20.20	0.134646020	0.136294784
20.40	0.134411690	0.135760114
20.60	0.134180180	0.135240093
20.80	0.134307300	0.134736993
21.00	0.134317170	0.134248945
21.20	0.134181800	0.133774514
21.40	0.134039450	0.133314665
21.60	0.133793830	0.132869864
21.80	0.133480720	0.132438892
22.00	0.133046040	0.132018664
22.20	0.132444690	0.131605998
22.40	0.131895050	0.131198940
22.60	0.131235520	0.130796043
22.80	0.130626480	0.130398309
23.00	0.130034250	0.130008200
23.20	0.129552410	0.129628399
23.40	0.128987550	0.129260610

23.60	0.128619550	0.128905945
23.80	0.128133810	0.128563145
24.00	0.127692300	0.128231803
24.20	0.127370980	0.127911938
24.40	0.126925820	0.127603963
24.60	0.126720960	0.127310549
24.80	0.126515930	0.127033382
25.00	0.126463440	0.126774302
25.20	0.126311970	0.126535456
25.40	0.126353480	0.126320031
25.60	0.126357200	0.126128454
25.80	0.126318570	0.125958897
26.00	0.126493470	0.125806646
26.20	0.126448000	0.125663728
26.40	0.126313090	0.125526302
26.60	0.126028500	0.125396447
26.80	0.125730640	0.125279755
27.00	0.125493140	0.125179643
27.20	0.125130040	0.125094348
27.40	0.125044820	0.125018407

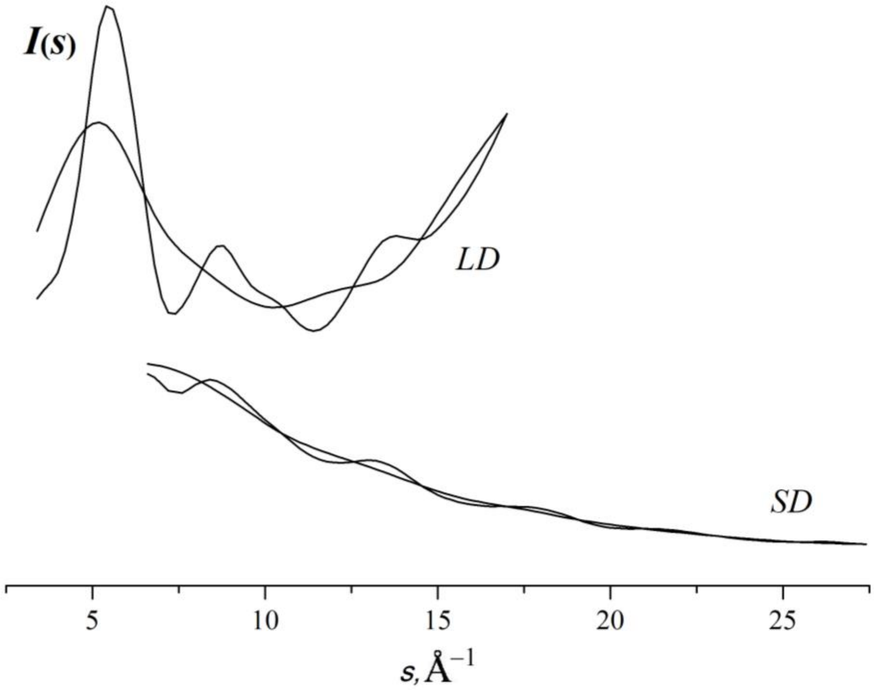

Figure S8. Experimental intensity curves *I(s)* of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6** with background lines for the long (LD) and short (SD) nozzle-to-film distances.

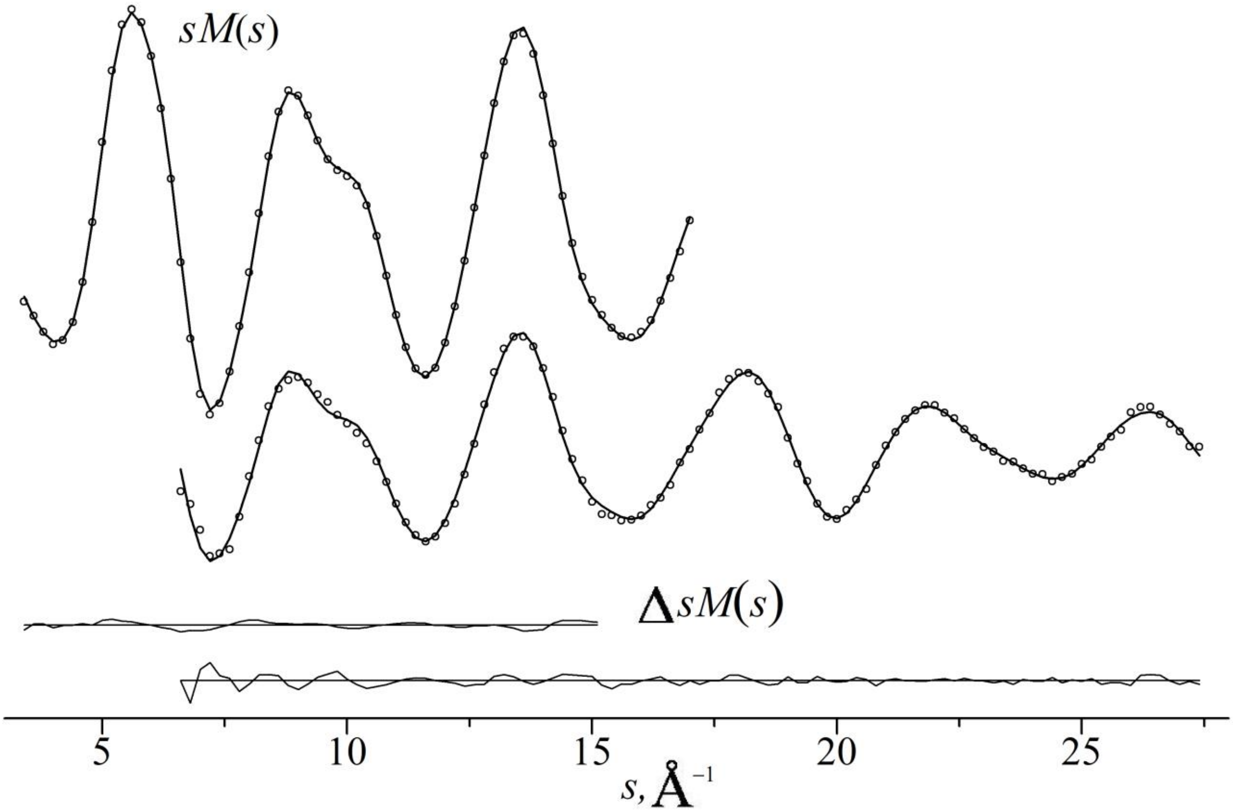

Figure S9. Experimental (circles) and theoretical (solid line) molecular intensity curves *sM(s)* with their difference curves *ΔsM(s)* of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6** for the long and short nozzle-to-film distances.

Table S5. Vibrational corrections $\Delta(r_{ij,h1} - r_{ij,a})$ to internuclear distances $r_{ij,a}$, theoretical $u_{ij,h1}$ and experimental $u_{ij,exp}$ vibrational amplitudes of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6** (*gauche-boat* conformer, 85%).

Term	r_a	$r_{h1} - r_a$ [a]	u_{h1} [b]	u_{exp} [c,d]
C(9)–H(21)	1.0882	0.0018	0.075	0.075[d]
C(9)–H(20)	1.0890	0.0019	0.076	0.076[d]
C(8)–H(18)	1.0892	0.0019	0.076	0.076[d]
C(8)–H(19)	1.0896	0.0018	0.076	0.076[d]
C(7)–H(17)	1.0922	0.0016	0.076	0.076[d]
C(6)–H(16)	1.0971	0.0015	0.077	0.077[d]
C(3)–H(13)	1.0973	0.0015	0.077	0.077[d]
C(3)–H(12)	1.0975	0.0013	0.077	0.077[d]
C(4)–H(15)	1.0992	0.0012	0.077	0.077[d]
C(2)–H(11)	1.0993	0.0012	0.077	0.077[d]
C(4)–H(14)	1.0995	0.0014	0.077	0.077[d]
C(2)–H(10)	1.0995	0.0014	0.077	0.077[d]
C(6)–N(5)	1.4488	-0.0006	0.050	0.052(4)[c1]
C(6)–N(1)	1.4553	-0.0006	0.050	0.052(4)[c1]
N(5)–C(4)	1.4819	0.0008	0.052	0.054(4)[c1]
N(1)–C(2)	1.4827	0.0008	0.052	0.054(4)[c1]
C(9)–C(7)	1.4890	0.0002	0.051	0.053(4)[c1]

C(9)–C(8)	1.4949	-0.0009	0.051	0.053(4)[c1]
C(8)–C(7)	1.5000	0.0002	0.052	0.054(4)[c1]
C(7)–C(6)	1.5067	0.0011	0.050	0.051(4)[c1]
N(5)–N(1)	1.5125	0.0033	0.056	0.058(4)[c1]
C(4)–C(3)	1.5376	0.0000	0.053	0.055(4)[c1]
C(2)–C(3)	1.5381	0.0000	0.053	0.055(4)[c1]
H(13)···H(12)	1.7603	0.0083	0.123	0.123[d]
H(10)···H(11)	1.7720	0.0082	0.123	0.123[d]
H(14)···H(15)	1.7724	0.0082	0.123	0.123[d]
H(19)···H(18)	1.8324	0.0063	0.120	0.120[d]
H(20)···H(21)	1.8362	0.0062	0.120	0.120[d]
N(5)···H(15)	2.0808	0.0064	0.104	0.104[d]
N(1)···H(11)	2.0815	0.0064	0.104	0.104[d]
N(1)···H(10)	2.1131	0.0066	0.106	0.106[d]
N(5)···H(14)	2.1136	0.0065	0.106	0.106[d]
N(5)···H(16)	2.1742	0.0068	0.101	0.101[d]
N(1)···H(16)	2.1776	0.0069	0.102	0.102[d]
C(6)···H(17)	2.1819	0.0045	0.104	0.104[d]
C(3)···H(15)	2.1870	0.0058	0.107	0.107[d]
C(3)···H(11)	2.1873	0.0058	0.107	0.107[d]
C(2)···H(12)	2.1874	0.0058	0.107	0.107[d]
C(4)···H(12)	2.1883	0.0058	0.107	0.107[d]
C(7)···H(16)	2.1895	0.0036	0.102	0.102[d]
C(2)···H(13)	2.1923	0.0065	0.108	0.108[d]
C(4)···H(13)	2.1935	0.0065	0.108	0.108[d]
C(7)···H(21)	2.1948	0.0102	0.106	0.106[d]
H(16)···H(12)	2.1979	0.0037	0.231	0.231[d]
C(9)···H(17)	2.1997	0.0099	0.105	0.105[d]
C(8)···H(17)	2.2044	0.0099	0.106	0.106[d]
C(9)···H(19)	2.2057	0.0098	0.106	0.106[d]
C(7)···H(20)	2.2079	0.0100	0.105	0.105[d]
C(8)···H(21)	2.2080	0.0095	0.105	0.105[d]
C(3)···H(14)	2.2090	0.0053	0.107	0.107[d]
C(3)···H(10)	2.2091	0.0053	0.107	0.107[d]
C(7)···H(19)	2.2123	0.0103	0.106	0.106[d]
C(8)···H(20)	2.2213	0.0088	0.106	0.106[d]
C(7)···H(18)	2.2232	0.0100	0.106	0.106[d]
C(9)···H(18)	2.2274	0.0088	0.106	0.106[d]
H(11)···H(13)	2.3901	0.0086	0.174	0.174[d]
H(15)···H(13)	2.3923	0.0087	0.174	0.174[d]
C(2)···C(4)	2.3994	0.0034	0.063	0.067(10)[c2]
H(10)···H(12)	2.4069	0.0076	0.175	0.175[d]
H(14)···H(12)	2.4091	0.0076	0.175	0.175[d]
N(5)···C(2)	2.4102	0.0044	0.059	0.063(10)[c2]
N(1)···C(4)	2.4149	0.0043	0.059	0.063(10)[c2]
C(6)···C(4)	2.4374	0.0024	0.067	0.071(10)[c2]
N(5)···C(3)	2.4399	0.0030	0.059	0.063(10)[c2]
C(6)···C(2)	2.4399	0.0024	0.067	0.071(10)[c2]
N(1)···C(3)	2.4438	0.0030	0.059	0.063(10)[c2]
H(17)···H(20)	2.4700	0.0199	0.175	0.175[d]
H(21)···H(19)	2.4713	0.0207	0.177	0.177[d]
H(17)···H(18)	2.4811	0.0200	0.176	0.176[d]

C(3)···H(16)	2.4979	0.0045	0.154	0.154[d]
H(20)···H(18)	2.5228	0.0185	0.177	0.177[d]
H(16)···H(17)	2.5309	0.0008	0.178	0.178[d]
C(7)···N(5)	2.5321	0.0047	0.068	0.072(10)[c2]
C(7)···N(1)	2.5478	0.0039	0.071	0.075(10)[c2]
C(2)···H(16)	2.5503	0.0096	0.145	0.145[d]
C(4)···H(16)	2.5515	0.0095	0.145	0.145[d]
C(8)···C(6)	2.5947	0.0049	0.076	0.080(10)[c2]
C(9)···C(6)	2.6004	0.0051	0.071	0.075(10)[c2]
N(5)···H(21)	2.6129	-0.0060	0.218	0.218[d]
H(10)···H(16)	2.6845	0.0207	0.233	0.233[d]
H(14)···H(16)	2.6877	0.0204	0.232	0.232[d]
C(6)···H(19)	2.7511	0.0148	0.161	0.161[d]
C(6)···C(3)	2.7526	0.0019	0.080	0.084(10)[c2]
C(6)···H(21)	2.7533	0.0149	0.156	0.156[d]
H(10)···H(13)	2.7955	0.0110	0.154	0.154[d]
H(14)···H(13)	2.7973	0.0110	0.154	0.154[d]
C(6)···H(14)	2.8173	0.0122	0.152	0.152[d]
C(6)···H(10)	2.8202	0.0122	0.153	0.153[d]
N(5)···H(19)	2.8581	0.0175	0.277	0.277[d]
C(6)···H(12)	2.8671	0.0085	0.182	0.182[d]
C(2)···H(15)	2.9257	0.0129	0.152	0.152[d]
C(4)···H(11)	2.9270	0.0130	0.152	0.152[d]
N(1)···H(21)	2.9426	0.0187	0.267	0.267[d]
C(9)···N(5)	2.9910	-0.0021	0.124	0.124[d]
N(5)···H(11)	2.9928	0.0138	0.137	0.137[d]
N(1)···H(15)	2.9944	0.0137	0.137	0.137[d]
N(5)···H(12)	2.9980	0.0102	0.137	0.137[d]
N(1)···H(12)	3.0017	0.0102	0.137	0.137[d]
H(11)···H(12)	3.0409	0.0160	0.130	0.130[d]
H(15)···H(12)	3.0423	0.0160	0.130	0.130[d]
H(11)···H(15)	3.0685	0.0231	0.255	0.255[d]
H(17)···H(21)	3.0755	0.0199	0.129	0.129[d]
H(17)···H(19)	3.0868	0.0199	0.130	0.130[d]
H(20)···H(19)	3.0945	0.0197	0.129	0.129[d]
H(21)···H(18)	3.1020	0.0194	0.129	0.129[d]
N(1)···H(17)	3.1146	0.0138	0.171	0.171[d]
C(8)···N(5)	3.1249	0.0060	0.156	0.156[d]
C(8)···H(16)	3.1613	0.0143	0.171	0.171[d]
C(9)···N(1)	3.1731	0.0075	0.150	0.150[d]
H(16)···H(19)	3.2354	0.0310	0.263	0.263[d]
N(5)···H(10)	3.2594	0.0144	0.108	0.108[d]
N(1)···H(14)	3.2652	0.0143	0.108	0.108[d]
C(4)···H(10)	3.3190	0.0136	0.102	0.102[d]
C(2)···H(14)	3.3195	0.0135	0.102	0.102[d]
N(5)···H(13)	3.3270	0.0140	0.105	0.105[d]
N(1)···H(13)	3.3295	0.0140	0.105	0.105[d]
C(6)···H(15)	3.3365	0.0114	0.101	0.101[d]
C(6)···H(11)	3.3402	0.0115	0.102	0.102[d]
N(5)···H(17)	3.4471	0.0210	0.105	0.105[d]
C(6)···H(18)	3.4787	0.0156	0.112	0.112[d]
C(6)···H(20)	3.4859	0.0160	0.109	0.109[d]

C(9)···H(16)	3.5105	0.0204	0.106	0.106[d]
H(16)···H(13)	3.5716	0.0147	0.175	0.175[d]
H(14)···H(19)	3.5975	-0.0188	0.303	0.303[d]
H(11)···H(16)	3.6082	0.0202	0.156	0.156[d]
H(15)···H(16)	3.6088	0.0200	0.156	0.156[d]
C(8)···N(1)	3.7025	0.0197	0.116	0.116[d]
C(7)···C(4)	3.7776	0.0082	0.076	0.076[d]
H(16)···H(21)	3.7814	0.0384	0.173	0.173[d]
C(7)···C(2)	3.7930	0.0072	0.077	0.077[d]
C(6)···H(13)	3.8223	0.0132	0.104	0.104[d]
C(4)···H(19)	3.8269	0.0023	0.261	0.261[d]
N(1)···H(19)	3.8400	0.0393	0.223	0.223[d]
H(16)···H(18)	3.8703	0.0173	0.201	0.201[d]
N(1)···H(20)	3.9416	0.0126	0.176	0.176[d]
H(10)···H(15)	3.9630	0.0240	0.157	0.157[d]
H(11)···H(14)	3.9643	0.0240	0.158	0.158[d]
C(7)···H(14)	3.9908	0.0154	0.168	0.168[d]
N(5)···H(20)	3.9963	0.0145	0.154	0.154[d]
C(7)···H(10)	4.0149	0.0137	0.168	0.168[d]
C(4)···H(21)	4.0393	0.0107	0.241	0.241[d]
H(10)···H(14)	4.0931	0.0252	0.160	0.160[d]
H(10)···H(17)	4.1429	0.0031	0.252	0.252[d]
N(5)···H(18)	4.1670	0.0225	0.175	0.175[d]
C(2)···H(17)	4.1963	0.0086	0.174	0.174[d]
C(8)···H(14)	4.2367	0.0008	0.227	0.227[d]
C(7)···C(3)	4.2549	0.0071	0.086	0.086[d]
C(7)···H(12)	4.2907	0.0101	0.198	0.198[d]
C(8)···C(4)	4.2997	0.0060	0.154	0.154[d]
H(16)···H(20)	4.3461	0.0319	0.138	0.138[d]
H(15)···H(21)	4.3776	0.0015	0.282	0.282[d]
C(2)···H(21)	4.3945	0.0259	0.258	0.258[d]
C(9)···C(4)	4.4184	0.0092	0.134	0.134[d]
H(14)···H(21)	4.4239	0.0346	0.319	0.319[d]
H(15)···H(19)	4.4306	0.0158	0.328	0.328[d]
C(7)···H(15)	4.5815	0.0192	0.115	0.115[d]
C(4)···H(17)	4.5870	0.0227	0.118	0.118[d]
C(7)···H(11)	4.5993	0.0181	0.116	0.116[d]
C(9)···C(2)	4.6185	0.0163	0.140	0.140[d]
N(1)···H(18)	4.6563	0.0329	0.120	0.120[d]
H(17)···H(12)	4.6706	0.0064	0.247	0.247[d]
C(9)···H(14)	4.6923	0.0207	0.211	0.211[d]
C(3)···H(17)	4.7907	0.0105	0.149	0.149[d]
H(11)···H(21)	4.7933	0.0271	0.329	0.329[d]
H(14)···H(17)	4.7947	0.0337	0.213	0.213[d]
C(3)···H(19)	4.8994	0.0207	0.231	0.231[d]
C(3)···H(21)	4.9473	0.0221	0.203	0.203[d]
C(9)···H(15)	4.9639	0.0127	0.184	0.184[d]
H(19)···H(12)	4.9650	0.0263	0.308	0.308[d]
C(8)···C(2)	4.9715	0.0240	0.095	0.095[d]
H(10)···H(21)	4.9757	0.0496	0.296	0.296[d]
C(8)···H(15)	4.9926	0.0181	0.207	0.207[d]
C(2)···H(19)	5.0003	0.0398	0.204	0.204[d]

C(9)···H(10)	5.0119	0.0307	0.199	0.199[d]
H(11)···H(17)	5.0406	0.0250	0.210	0.210[d]
H(14)···H(18)	5.1105	0.0149	0.272	0.272[d]
C(8)···C(3)	5.1471	0.0150	0.128	0.128[d]
C(8)···H(12)	5.1753	0.0180	0.233	0.233[d]
C(9)···C(3)	5.1783	0.0159	0.105	0.105[d]
C(9)···H(11)	5.1929	0.0228	0.203	0.203[d]
C(4)···H(18)	5.2756	0.0230	0.189	0.189[d]
C(7)···H(13)	5.3217	0.0206	0.107	0.107[d]
C(8)···H(10)	5.3433	0.0367	0.166	0.166[d]
C(2)···H(20)	5.3796	0.0245	0.183	0.183[d]
H(21)···H(12)	5.3991	0.0409	0.238	0.238[d]
C(9)···H(12)	5.4348	0.0261	0.188	0.188[d]
C(4)···H(20)	5.4419	0.0270	0.155	0.155[d]
H(15)···H(17)	5.4600	0.0389	0.138	0.138[d]
H(10)···H(19)	5.5294	0.0569	0.223	0.223[d]
H(10)···H(20)	5.6492	0.0359	0.249	0.249[d]
C(8)···H(11)	5.7391	0.0383	0.154	0.154[d]
H(11)···H(19)	5.7402	0.0567	0.266	0.266[d]
H(14)···H(20)	5.7503	0.0405	0.216	0.216[d]
H(21)···H(13)	5.8450	0.0320	0.232	0.232[d]
H(17)···H(13)	5.8618	0.0251	0.166	0.166[d]
H(19)···H(13)	5.8633	0.0325	0.254	0.254[d]
C(2)···H(18)	5.8861	0.0382	0.120	0.120[d]
H(11)···H(20)	5.9010	0.0292	0.240	0.240[d]
H(18)···H(12)	5.9569	0.0250	0.267	0.267[d]
H(15)···H(20)	5.9716	0.0326	0.215	0.215[d]
H(15)···H(18)	6.0097	0.0398	0.240	0.240[d]
C(3)···H(18)	6.0538	0.0282	0.161	0.161[d]
C(3)···H(20)	6.1001	0.0300	0.136	0.136[d]
H(10)···H(18)	6.1396	0.0487	0.211	0.211[d]
C(9)···H(13)	6.1729	0.0293	0.134	0.134[d]
C(8)···H(13)	6.1800	0.0293	0.150	0.150[d]
H(20)···H(12)	6.3360	0.0399	0.208	0.208[d]
H(11)···H(18)	6.7008	0.0556	0.151	0.151[d]
H(20)···H(13)	7.0953	0.0446	0.162	0.162[d]
H(18)···H(13)	7.1035	0.0445	0.179	0.179[d]

[a] Calculated with B3LYP/cc-pVTZ quadratic force field.
[b] Calculated value (from B3LYP/cc-pVTZ quadratic force field) .
[c] Amplitudes with equal superscripts were refined in one group. Differences between amplitudes in each group were fixed at the corresponding calculated values (from B3LYP /cc-pVTZ quadratic force field). Estimated errors given in parentheses are 2.5σ. [d] Fixed at the calculated u_{h1} value.

Table S6. Vibrational corrections $\Delta(r_{ij,h1} - r_{ij,a})$ to internuclear distances $r_{ij,a}$, theoretical $u_{ij,h1}$ and experimental $u_{ij,exp}$ vibrational amplitudes of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6** (*anti-boat* conformer, 15%).

Term	r_a	$r_{h1} - r_a$ [a]	u_{h1} [b]	u_{exp} [c,d]
C(9)–H(21)	1.0888	0.0019	0.076	0.076[d]
C(8)–H(19)	1.0888	0.0019	0.076	0.076[d]
C(7)–H(17)	1.0896	0.0016	0.076	0.076[d]
C(8)–H(18)	1.0903	0.0018	0.076	0.076[d]
C(9)–H(20)	1.0903	0.0018	0.076	0.076[d]
C(3)–H(13)	1.0973	0.0015	0.077	0.077[d]
C(3)–H(12)	1.0977	0.0013	0.077	0.077[d]
C(6)–H(16)	1.0980	0.0015	0.077	0.077[d]
C(4)–H(15)	1.0993	0.0012	0.077	0.077[d]
C(2)–H(11)	1.0993	0.0012	0.077	0.077[d]
C(2)–H(10)	1.0995	0.0014	0.077	0.077[d]
C(4)–H(14)	1.0995	0.0014	0.077	0.077[d]
C(6)–N(1)	1.4519	-0.0006	0.050	0.052(4)[c1]
C(6)–N(5)	1.4519	-0.0006	0.050	0.052(4)[c1]
N(5)–C(4)	1.4823	0.0008	0.052	0.054(4)[c1]
N(1)–C(2)	1.4823	0.0008	0.052	0.054(4)[c1]
C(9)–C(8)	1.4953	-0.0009	0.051	0.053(4)[c1]
C(8)–C(7)	1.4962	0.0003	0.051	0.053(4)[c1]
C(9)–C(7)	1.4962	0.0003	0.051	0.053(4)[c1]
C(7)–C(6)	1.5006	0.0011	0.049	0.051(4)[c1]
N(5)–N(1)	1.5148	0.0032	0.056	0.058(4)[c1]
C(2)–C(3)	1.5379	0.0000	0.053	0.055(4)[c1]
C(4)–C(3)	1.5379	0.0000	0.053	0.055(4)[c1]
H(13)···H(12)	1.7599	0.0084	0.123	0.123[d]
H(14)···H(15)	1.7720	0.0082	0.123	0.123[d]
H(10)···H(11)	1.7720	0.0082	0.123	0.123[d]
H(19)···H(18)	1.8259	0.0065	0.120	0.120[d]
H(20)···H(21)	1.8259	0.0065	0.120	0.120[d]
N(5)···H(15)	2.0816	0.0063	0.104	0.104[d]
N(1)···H(11)	2.0816	0.0063	0.104	0.104[d]
N(1)···H(10)	2.1133	0.0066	0.106	0.106[d]
N(5)···H(14)	2.1133	0.0066	0.106	0.106[d]
C(6)···H(17)	2.1721	0.0057	0.104	0.104[d]
N(5)···H(16)	2.1819	0.0070	0.102	0.102[d]
N(1)···H(16)	2.1819	0.0070	0.102	0.102[d]
C(3)···H(11)	2.1869	0.0058	0.107	0.107[d]
C(3)···H(15)	2.1869	0.0058	0.107	0.107[d]
C(7)···H(16)	2.1890	0.0043	0.102	0.102[d]
C(4)···H(12)	2.1898	0.0058	0.107	0.107[d]
C(2)···H(12)	2.1898	0.0058	0.107	0.107[d]
C(2)···H(13)	2.1917	0.0065	0.108	0.108[d]
C(4)···H(13)	2.1917	0.0065	0.108	0.108[d]
H(16)···H(12)	2.2037	0.0037	0.231	0.231[d]
C(9)···H(17)	2.2084	0.0103	0.105	0.105[d]
C(8)···H(17)	2.2084	0.0103	0.105	0.105[d]
C(3)···H(10)	2.2096	0.0053	0.107	0.107[d]

C(3)···H(14)	2.2096	0.0053	0.107	0.107[d]
C(9)···H(18)	2.2152	0.0095	0.106	0.106[d]
C(8)···H(20)	2.2152	0.0095	0.106	0.106[d]
C(7)···H(21)	2.2168	0.0100	0.106	0.106[d]
C(7)···H(19)	2.2168	0.0100	0.106	0.106[d]
C(7)···H(18)	2.2181	0.0100	0.106	0.106[d]
C(7)···H(20)	2.2181	0.0100	0.106	0.106[d]
C(8)···H(21)	2.2232	0.0087	0.106	0.106[d]
C(9)···H(19)	2.2232	0.0087	0.106	0.106[d]
H(11)···H(13)	2.3893	0.0087	0.174	0.174[d]
H(15)···H(13)	2.3893	0.0087	0.174	0.174[d]
C(2)···C(4)	2.3988	0.0034	0.063	0.067(10)[c2]
H(14)···H(12)	2.4116	0.0076	0.175	0.175[d]
H(10)···H(12)	2.4116	0.0076	0.175	0.175[d]
N(1)···C(4)	2.4135	0.0043	0.060	0.064(10)[c2]
N(5)···C(2)	2.4135	0.0043	0.060	0.064(10)[c2]
C(6)···C(2)	2.4383	0.0025	0.067	0.071(10)[c2]
C(6)···C(4)	2.4383	0.0025	0.067	0.071(10)[c2]
N(1)···C(3)	2.4419	0.0029	0.059	0.063(10)[c2]
N(5)···C(3)	2.4419	0.0029	0.059	0.063(10)[c2]
H(17)···H(21)	2.4860	0.0205	0.176	0.176[d]
H(17)···H(19)	2.4860	0.0205	0.176	0.176[d]
H(20)···H(18)	2.4932	0.0205	0.178	0.178[d]
C(3)···H(16)	2.5046	0.0048	0.155	0.155[d]
H(21)···H(19)	2.5191	0.0183	0.177	0.177[d]
C(7)···N(1)	2.5236	0.0042	0.071	0.075(10)[c2]
C(7)···N(5)	2.5236	0.0042	0.071	0.075(10)[c2]
C(4)···H(16)	2.5601	0.0098	0.146	0.146[d]
C(2)···H(16)	2.5601	0.0098	0.146	0.146[d]
C(9)···C(6)	2.5878	0.0045	0.076	0.080(10)[c2]
C(8)···C(6)	2.5878	0.0045	0.076	0.080(10)[c2]
H(16)···H(20)	2.5898	-0.0008	0.256	0.256[d]
H(16)···H(18)	2.5898	-0.0008	0.256	0.256[d]
H(14)···H(16)	2.6968	0.0207	0.233	0.233[d]
H(10)···H(16)	2.6968	0.0207	0.233	0.233[d]
N(1)···H(17)	2.7157	0.0016	0.166	0.166[d]
N(5)···H(17)	2.7157	0.0016	0.166	0.166[d]
C(6)···C(3)	2.7495	0.0020	0.080	0.084(10)[c2]
C(6)···H(20)	2.7595	0.0134	0.163	0.163[d]
C(6)···H(18)	2.7595	0.0134	0.163	0.163[d]
H(10)···H(13)	2.7947	0.0110	0.154	0.154[d]
H(14)···H(13)	2.7947	0.0110	0.154	0.154[d]
C(9)···H(16)	2.7961	-0.0028	0.165	0.165[d]
C(8)···H(16)	2.7961	-0.0028	0.165	0.165[d]
C(6)···H(10)	2.8211	0.0122	0.153	0.153[d]
C(6)···H(14)	2.8211	0.0122	0.153	0.153[d]
C(6)···H(12)	2.8650	0.0085	0.181	0.181[d]
C(4)···H(11)	2.9225	0.0129	0.152	0.152[d]
C(2)···H(15)	2.9225	0.0129	0.152	0.152[d]
N(1)···H(15)	2.9928	0.0137	0.137	0.137[d]
N(5)···H(11)	2.9928	0.0137	0.137	0.137[d]
N(5)···H(12)	3.0007	0.0101	0.138	0.138[d]

N(1)···H(12)	3.0007	0.0101	0.138	0.138[d]
H(15)···H(12)	3.0433	0.0160	0.130	0.130[d]
H(11)···H(12)	3.0433	0.0160	0.130	0.130[d]
H(11)···H(15)	3.0599	0.0229	0.254	0.254[d]
H(16)···H(17)	3.0925	0.0216	0.123	0.123[d]
H(17)···H(20)	3.0934	0.0200	0.130	0.130[d]
H(17)···H(18)	3.0934	0.0200	0.130	0.130[d]
H(21)···H(18)	3.1006	0.0196	0.130	0.130[d]
H(20)···H(19)	3.1006	0.0196	0.130	0.130[d]
N(1)···H(14)	3.2649	0.0142	0.108	0.108[d]
N(5)···H(10)	3.2649	0.0142	0.108	0.108[d]
C(4)···H(10)	3.3207	0.0134	0.102	0.102[d]
C(2)···H(14)	3.3207	0.0134	0.102	0.102[d]
N(1)···H(13)	3.3281	0.0138	0.105	0.105[d]
N(5)···H(13)	3.3281	0.0138	0.105	0.105[d]
C(6)···H(15)	3.3378	0.0115	0.102	0.102[d]
C(6)···H(11)	3.3378	0.0115	0.102	0.102[d]
C(6)···H(21)	3.4750	0.0160	0.111	0.111[d]
C(6)···H(19)	3.4750	0.0160	0.111	0.111[d]
C(9)···N(1)	3.5768	0.0185	0.152	0.152[d]
C(8)···N(5)	3.5768	0.0185	0.152	0.152[d]
H(16)···H(13)	3.5781	0.0150	0.176	0.176[d]
H(15)···H(16)	3.6174	0.0204	0.156	0.156[d]
H(11)···H(16)	3.6174	0.0204	0.156	0.156[d]
N(1)···H(20)	3.6976	0.0342	0.258	0.258[d]
N(5)···H(18)	3.6976	0.0342	0.258	0.258[d]
C(7)···C(4)	3.7749	0.0080	0.077	0.077[d]
C(7)···C(2)	3.7749	0.0080	0.077	0.077[d]
H(16)···H(21)	3.8146	0.0143	0.182	0.182[d]
H(16)···H(19)	3.8146	0.0143	0.182	0.182[d]
C(6)···H(13)	3.8192	0.0133	0.104	0.104[d]
C(9)···N(5)	3.8767	0.0214	0.075	0.075[d]
C(8)···N(1)	3.8767	0.0214	0.075	0.075[d]
H(10)···H(15)	3.9610	0.0239	0.157	0.157[d]
H(11)···H(14)	3.9610	0.0239	0.157	0.157[d]
C(7)···H(14)	3.9997	0.0151	0.168	0.168[d]
C(7)···H(10)	3.9997	0.0151	0.168	0.168[d]
H(10)···H(20)	4.0808	0.0151	0.159	0.392[d]
H(14)···H(18)	4.0808	0.0151	0.392	0.392[d]
H(10)···H(14)	4.0980	0.0249	0.392	0.159[d]
C(2)···H(17)	4.1467	0.0122	0.162	0.162[d]
C(4)···H(17)	4.1467	0.0122	0.162	0.162[d]
N(5)···H(20)	4.1754	0.0367	0.161	0.161[d]
N(1)···H(18)	4.1754	0.0367	0.161	0.161[d]
C(7)···C(3)	4.2455	0.0077	0.200	0.085[d]
N(1)···H(21)	4.2457	0.0262	0.200	0.200[d]
N(5)···H(19)	4.2457	0.0262	0.085	0.200[d]
C(7)···H(12)	4.2880	0.0110	0.196	0.196[d]
C(2)···H(20)	4.4103	0.0233	0.293	0.293[d]
C(4)···H(18)	4.4103	0.0233	0.293	0.293[d]
C(9)···H(10)	4.4889	0.0127	0.220	0.269[d]
C(8)···H(14)	4.4889	0.0127	0.220	0.269[d]

H(10)···H(17)	4.4895	0.0265	0.269	0.220[d]
H(14)···H(17)	4.4895	0.0265	0.269	0.220[d]
H(20)···H(12)	4.5500	0.0000	0.116	0.331[d]
H(18)···H(12)	4.5500	0.0000	0.116	0.331[d]
C(7)···H(15)	4.5767	0.0187	0.331	0.116[d]
C(7)···H(11)	4.5767	0.0187	0.331	0.116[d]
C(9)···C(2)	4.6019	0.0157	0.170	0.170[d]
C(8)···C(4)	4.6019	0.0157	0.170	0.170[d]
N(5)···H(21)	4.6661	0.0351	0.130	0.130[d]
N(1)···H(19)	4.6661	0.0351	0.130	0.130[d]
H(11)···H(17)	4.7511	0.0156	0.209	0.209[d]
H(15)···H(17)	4.7511	0.0156	0.209	0.209[d]
C(3)···H(17)	4.7768	0.0159	0.136	0.136[d]
C(3)···H(20)	4.9195	0.0154	0.248	0.248[d]
C(3)···H(18)	4.9195	0.0154	0.248	0.248[d]
C(9)···H(12)	4.9471	0.0058	0.249	0.249[d]
C(8)···H(12)	4.9471	0.0058	0.249	0.249[d]
C(9)···C(4)	4.9676	0.0236	0.105	0.105[d]
C(8)···C(2)	4.9676	0.0236	0.105	0.105[d]
H(17)···H(12)	5.0192	0.0277	0.205	0.205[d]
C(4)···H(20)	5.0324	0.0366	0.209	0.209[d]
C(2)···H(18)	5.0324	0.0366	0.209	0.209[d]
C(9)···H(14)	5.1082	0.0324	0.226	0.226[d]
C(8)···H(10)	5.1082	0.0324	0.226	0.226[d]
C(9)···C(3)	5.1457	0.0131	0.141	0.141[d]
C(8)···C(3)	5.1457	0.0131	0.141	0.141[d]
H(14)···H(20)	5.1586	0.0510	0.320	0.320[d]
H(10)···H(18)	5.1586	0.0510	0.320	0.320[d]
H(10)···H(21)	5.1947	0.0175	0.290	0.290[d]
H(14)···H(19)	5.1947	0.0175	0.290	0.290[d]
C(7)···H(13)	5.3114	0.0210	0.107	0.107[d]
H(11)···H(20)	5.3482	0.0471	0.208	0.334[d]
H(15)···H(18)	5.3482	0.0471	0.208	0.334[d]
C(2)···H(21)	5.3499	0.0255	0.334	0.208[d]
C(4)···H(19)	5.3499	0.0255	0.334	0.208[d]
C(9)···H(11)	5.4724	0.0341	0.206	0.206[d]
C(8)···H(15)	5.4724	0.0341	0.206	0.206[d]
H(17)···H(13)	5.7841	0.0283	0.159	0.159[d]
C(9)···H(15)	5.8688	0.0413	0.120	0.120[d]
C(8)···H(11)	5.8688	0.0413	0.120	0.120[d]
C(4)···H(21)	5.8749	0.0404	0.121	0.121[d]
C(2)···H(19)	5.8749	0.0404	0.121	0.121[d]
H(21)···H(12)	5.9320	0.0245	0.261	0.261[d]
H(19)···H(12)	5.9320	0.0245	0.261	0.261[d]
H(20)···H(13)	5.9598	0.0297	0.271	0.271[d]
H(18)···H(13)	5.9598	0.0297	0.271	0.271[d]
H(15)···H(20)	6.0138	0.0572	0.206	0.206[d]
H(11)···H(18)	6.0139	0.0572	0.206	0.206[d]
C(3)···H(21)	6.0631	0.0294	0.162	0.162[d]
C(3)···H(19)	6.0632	0.0294	0.162	0.162[d]
H(14)···H(21)	6.0834	0.0508	0.213	0.213[d]
H(10)···H(19)	6.0834	0.0508	0.213	0.213[d]

H(11)···H(21)	6.1184	0.0431	0.259	0.259[d]
H(15)···H(19)	6.1184	0.0431	0.259	0.259[d]
C(9)···H(13)	6.2195	0.0286	0.161	0.161[d]
C(8)···H(13)	6.2195	0.0286	0.161	0.161[d]
H(15)···H(21)	6.7080	0.0585	0.155	0.155[d]
H(11)···H(19)	6.7080	0.0585	0.155	0.155[d]
H(21)···H(13)	7.1220	0.0460	0.182	0.182[d]
H(19)···H(13)	7.1220	0.0460	0.182	0.182[d]

[a] Calculated with B3LYP/cc-pVTZ quadratic force field.
[b] Calculated value (from B3LYP/cc-pVTZ quadratic force field) .
[c] Amplitudes with equal superscripts were refined in one group. Differences between amplitudes in each group were fixed at the corresponding calculated values (from B3LYP /cc-pVTZ quadratic force field). Estimated errors given in parentheses are 2.5σ. [d] Fixed at the calculated u_{h1} value.

Table S7. Cartesian coordinates for refined structure of *gauche-boat* conformer 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6**

Atom	Mass	X	Y	Z
C	12.0000000	2.540663872385	-0.343943859910	0.665132394619
C	12.0000000	2.660404532595	0.725111890772	-0.371658485445
C	12.0000000	1.714272894547	-0.421873429574	-0.571312564251
C	12.0000000	0.227208515169	-0.177635479586	-0.521906308633
N	14.0030740	-0.309089768438	0.555526210912	0.605909598787
N	14.0030740	-0.577413434755	-0.926079452820	0.431215407649
C	12.0000000	-1.987610743932	-1.068584027855	-0.006554442398
C	12.0000000	-1.560268019925	1.279047664135	0.275338845769
C	12.0000000	-2.483721617193	0.308439287129	-0.479240809264
H	1.0078250	-2.049812389636	-1.840884796892	-0.788706729260
H	1.0078250	-2.558356779741	-1.422637549926	0.865163419609
H	1.0078250	-1.317849651656	2.182807433573	-0.304642018899
H	1.0078250	-2.006788750138	1.597450106796	1.229365344979
H	1.0078250	-0.220227844303	0.018105963842	-1.505982525997
H	1.0078250	2.007506965231	-1.169286717654	-1.314059749274
H	1.0078250	3.359817949189	-1.056154705679	0.773533496677
H	1.0078250	2.017837190401	-0.091118974457	1.587465161891
H	1.0078250	2.223750702077	1.697165686938	-0.135822358608
H	1.0078250	3.559706734627	0.764600049859	-0.988120910199
H	1.0078250	-3.542135495965	0.469962415960	-0.232190507981
H	1.0078250	-2.383947193198	0.419846843930	-1.567886090889

Table S8. Cartesian coordinates (˚A) for refined structure of *anti-boat* conformer 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane

Atom	Mass	X	Y	Z
C	12.000000	2.751436362800	0.747221146125	0.372666695335
C	12.000000	2.751439588650	-0.747220198038	0.372664239870
C	12.000000	1.723584738154	-0.000000446095	-0.417655788546
C	12.000000	0.292102949225	-0.000000130504	0.036357480132
N	14.003074	-0.664986849582	-0.758993697475	-0.747412903064
N	14.003074	-0.664986717788	0.758992942143	-0.747413542700
C	12.000000	-1.832624131282	1.201104232895	0.053003370838
C	12.000000	-1.832624339844	-1.201104110930	0.053004383060
C	12.000000	-2.328156678312	0.000000450712	0.875810487162
H	1.007825	-1.543304568862	2.061477305298	0.675957163832
H	1.007825	-2.598776695548	1.541374427968	-0.659952732319
H	1.007825	-1.543304926822	-2.061476708582	0.675958901126
H	1.007825	-2.598776963197	-1.541374773805	-0.659951433337
H	1.007825	0.168405288400	-0.000004940302	1.128924159866
H	1.007825	1.832275737679	0.000004357402	-1.503370250256
H	1.007825	2.426680215614	1.256849262815	1.282386488091
H	1.007825	3.537519295093	1.268689833283	-0.174794287818
H	1.007825	3.537524772179	-1.268683692537	-0.174798456890
H	1.007825	2.426685641604	-1.256852706194	1.282382357913
H	1.007825	-3.421750735831	0.000001812774	0.982483411008
H	1.007825	-1.903859315757	-0.000004925276	1.889601189775

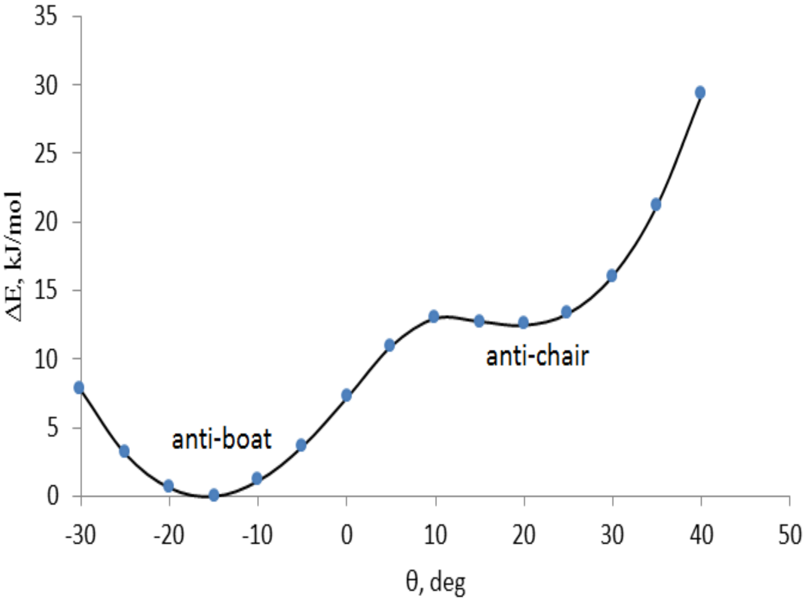

Figure S10. Potential energy curve of nonplanar ring puckering deformation of the bicyclic moiety of 6-cyclopropyl-1,5diazabicyclo[3.1.0]hexane **6** as a function of *θ* (N1–N5–C4-C3 dihedral angle) according to B3LYP/ cc-pVTZ calculation.

Table S9. Molecular structure of *anti-boat* and *gauche-boat* conformers of 6-cyclopropyl-1,5-diazabicyclo[3.1.0]hexane **6** obtained by GED data and quantum chemical calculations

Parameter [a]	GED, mixture of conformers		B3LYP/cc-pVTZ		MP2/cc-pVTZ	
	anti-boat (15%)	*gauche-boat (85%)*	*anti-boat*	*gauche-boat*	*anti-boat*	*gauche-boat*
	$r_{h1}(\angle_{h1})$ [b]		$r_e(\angle_e)$		$r_e(\angle_e)$	
C(8)-C(9)	1.494(11) [b1]	1.494(11) [b1]	1.504	1.503	1.505	1.504
C(7)-C(9)	1.496(11) [b1]	1.489(11) [b1]	1.506	1.499	1.505	1.498
C(7)-C(8)	1.496(11) [b1]	1.500(11) [b1]	1.506	1.510	1.505	1.509
C(6)-C(7)	1.502(21) [b2]	1.508(21) [b2]	1.487	1.493	1.478	1.485
N(5)-C(6)	1.451(21) [b3]	1.448(21) [b3]	1.447	1.444	1.449	1.447
N(1)-C(6)	1.451(21) [b3]	1.455(21) [b3]	1.447	1.451	1.449	1.453
N(1)-C(2)	1.483(18) [b4]	1.483(18) [b4]	1.477	1.477	1.475	1.476
C(4)-N(5)	1.483(18) [b4]	1.483(18) [b4]	1.477	1.476	1.475	1.475
C(3)-C(4)	1.538 [c]	1.538 [c]	1.538	1.538	1.530	1.531
C(2)-C(3)	1.538 [c]	1.538 [c]	1.538	1.538	1.530	1.531
N(1)-N(5)	1.518(17) [dep]	1.516(17) [dep]	1.509	1.507	1.519	1.517
$(C\text{-}H)_{average}$	1.097(4) [e]	1.096(4) [e]	1.087	1.086	1.085	1.085
N(5)-C(6)-C(7)	117.7(9) [b5]	118.2(9) [b5]	117.7	118.6	117.5	116.9
N(1)-C(6)-C(7)	117.7(9) [b5]	118.9(9) [b5]	117.7	119.3	117.5	118.6
C(2)-N(1)-C(6)	112.6(20) [b6]	112.5(20) [b6]	112.6	113.2	111.9	111.8
C(4)-N(5)-C(6)	112.6(20) [b6]	112.7(20) [b6]	112.6	113.5	111.9	112.0
C(8)-C(9)-C(7)	60.0(1) [dep]	60.4(1) [dep]	60.0	60.4	60.0	60.4
C(9)-C(7)-C(8)	59.9(1) [dep]	60.0(1) [dep]	59.9	60.0	60.0	60.0
C(2)-C(3)-C(4)	102.7(27) [dep]	102.7(27) [dep]	102.4	102.4	101.8	101.9
N(1)- C(2)-C(3)	108.0(21) [dep]	108.1(21) [dep]	108.0	108.1	108.2	108.3
N(5)-C(4)-C(3)	108.0(21) [dep]	108.0(21) [dep]	108.0	108.0	108.2	108.1
N(1)-N(5)-C(4)	107.3(9) [dep]	107.6(9) [dep]	107.5	107.7	106.9	107.2
N(5)-N(1)-C(2)	107.3(9) [dep]	107.2(9) [dep]	107.5	107.4	106.9	106.8
N(1)-N(5)-C(6)	58.5(3) [dep]	58.7(3) [dep]	58.6	58.9	58.4	58.7
N(5)-N(1)-C(6)	58.5(3) [dep]	58.3(3) [dep]	58.6	58.4	58.4	58.3
N(1)-C(6)-N(5)	63.1(6) [dep]	63.0(6) [dep]	62.8	62.7	63.2	63.1
N(5)-N(1)-C(2)-C(3)	15.8(7) [dep]	15.5(7) [dep]	15.9	15.5	17.6	17.2
N(1)-N(5)-C(4)-C(3)	-15.8(7) [dep]	-15.7(7) [dep]	-15.9	-15.8	-17.6	-17.4
N(5)-C(6)-C(7)-C(8)	-108.7	-50.2	-108.7	-50.2	-109.1	-46.1
N(1)-C(6)-C(7)-C(8)	178.9	-123.2	178.9	-123.2	178.4	-118.6
C(3)-C(4)-N(5)-C(6)	46.8	47.2	46.8	47.2	44.6	45.1
N(1)-C(2)-C(3)-C(4)	-24.6	-24.2	-24.6	-24.2	-27.2	-26.8
R_{factor}	5.3					

[a] Bond lengths (r_{h1} for GED and r_e for theoretical calculations) are in Å, bond angles ($\angle_{h1}$ for GED and $\angle_e$ for theoretical calculations) and torsional angles are in degrees. The total disagreement factor (R_{factor}) are given in %. [b] Values in parentheses are estimated errors (2.5σ). The same numeric superscripts indicate that these parameters were refined in one group; differences between parameters in the group were assumed at the values from B3LYP/cc-pVTZ calculation. [c] Assumed at the value from B3LYP/cc-pVTZ calculation. [dep] Dependent parameters. [e] All C–H bond lengths were refined in one group; their average value is given in this Table.