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6-Phenyl-1,5-diazabicyclo[3.1.0]hexane: structure variations going from gas to crystal phase

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Specimens of 6-phenyl-1,5-diazabicyclo[3.1.0]hexane were synthesized in the Institute of Organic Chemistry, Russian Academy of Sciences. The agreement with the previously published NMR and IR data,[S1,S2] as well as mass spectra,[S1] have proven the high purity of the substance (99.9%). The GED experiment was carried out with the use of the EG-100M electron diffraction apparatus.[S3] The main parameters are listed in Table S1. The diffraction patterns were digitized with the wedge calibrated Epson Perfection 4870 Scanner.

Table S1. GED experiments characteristics.

Nozzle-to-photofilm distance, mm	362.3	193.9
Beam current, μA	1.5	2.0
Exposure time, s	35, 40, 35	45, 45, 45
Nozzle temperature, K	367	367
Residual gas pressure, mm Hg	$4.0 \cdot 10^{-5}$	$4.0 \cdot 10^{-5}$
Number of the diffraction patterns (substance/ CCl_4 standard)	3 / 2	3 /2
Wavelength of electrons (λ), Å	0.04975	0.05013
Scattering variable range (s) [a] with an *increment* of 0.2 ($Å^{-1}$)	4.0÷16.8	7.0÷30.0

[a] Scattering parameter (s) is defined as $4\pi\lambda^{-1}sin(\theta/2)$, where θ is the scattering angle and λ is electron beam wavelength

Molecular GED model of the title compound was based on MP2/cc-pVTZ geometry and force field values:

21 internuclear distances (1-6 refined(group 1); 1-5 fixed; 4-5 refined(2)); 3-4 refined(3); 6-13 fixed; 7-6 refined(3); 4-18 fixed; 4-19 fixed; 3-16 fixed; 3-17 fixed; 7-8 refined(4); 8-9 refined(4); 10-9 refined(4); 10-11 refined(4); 11-12 refined(4); 7-12 refined(4); 8-20 fixed; 9-21 fixed; 10-22 fixed; 11-23 fixed; 12-24 fixed);

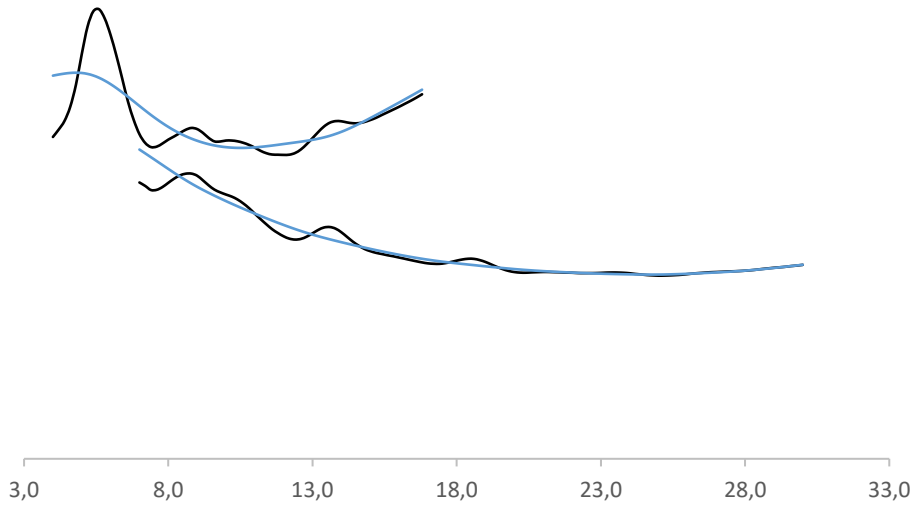
18 bond angles (1-5-4 refined(5); 1-6-13 refined(6); 1-6-7 refined(7); 5-4-18 refined(6); 3-4-18 refined(6); 5-4-19 refined(6); 3-4-19 refined(6); 4-3-16 refined(6); 4-3-17 refined(6); 6-7-8 refined(8); 7-8-9 refined(8); 8-9-10 refined(8); 9-10-11 refined(8); 9-8-20 refined(6); 9-10-21 refined(6); 11-10-22 refined(6); 12-11-23 refined(6); 7-12-24 refined(6));

and 12 dihedral angles (6-1-5-4 (fixed); 5-4-2-3 refined(9); 8-7-6-13 = 180º; 6-7-8-9 = 180º; 7-8-9-10 = 0º; 8-9-10-11 = 0º; 8-7-11-12 = 180º; 20-8-9-10 = 180º; 21-9-10-11 = 180º; 7-12-11-23 = 180º; 24-12-7-8 = 180º; 22-10-11-12 = 180º).

Bond distances with H atom (and N-N bond length) were fixed during GED refinement.

When all parameters were fixed at MP2/cc-pVTZ values, R_f = 12.5, 12.6 and 19.0% for boat, exo-chair and endo-chair conformer models. When vibrational amplitudes (u_{ij}) were not refined and other structural parameters were refined, the disagreement factor R_f was of 7.8, 8.4, and 10.0% for the boat, *exo*-chair, and *endo*-chair single-conformer PhDBH models, respectively.

Table S2. Total scattering intensities $I(s)$ and background lines $I^b(s)$ for PhDBH.



$I(s)$ and $I^b(s)$ curves of long nozzle-to-photofilm distance

s, Å^{-1}	$I(s)$	$I^b(s)$
4.0	0.398	0.474
4.2	0.407	0.475
4.4	0.418	0.477
4.6	0.435	0.477
4.8	0.463	0.478
5.0	0.500	0.477
5.2	0.535	0.476
5.4	0.554	0.474
5.6	0.556	0.471
5.8	0.544	0.468
6.0	0.524	0.463
6.2	0.499	0.459
6.4	0.471	0.453
6.6	0.442	0.448
6.8	0.419	0.442
7.0	0.402	0.437
7.2	0.391	0.431
7.4	0.386	0.425
7.6	0.386	0.420
7.8	0.390	0.415
8.0	0.395	0.411
8.2	0.399	0.406
8.4	0.403	0.403
8.6	0.407	0.399
8.8	0.409	0.396
9.0	0.408	0.393
9.2	0.403	0.391
9.4	0.397	0.389

9.6	0.393	0.388
9.8	0.393	0.386
10.0	0.394	0.386
10.2	0.394	0.385
10.4	0.393	0.385
10.6	0.391	0.385
10.8	0.388	0.385
11.0	0.385	0.385
11.2	0.381	0.386
11.4	0.378	0.387
11.6	0.376	0.388
11.8	0.376	0.388
12.0	0.376	0.389
12.2	0.376	0.390
12.4	0.378	0.391
12.6	0.383	0.392
12.8	0.389	0.393
13.0	0.397	0.395
13.2	0.404	0.396
13.4	0.411	0.398
13.6	0.416	0.400
13.8	0.418	0.402
14.0	0.418	0.404
14.2	0.416	0.407
14.4	0.415	0.411
14.6	0.415	0.414
14.8	0.417	0.418
15.0	0.419	0.421
15.2	0.422	0.425
15.4	0.425	0.429
15.6	0.429	0.433
15.8	0.432	0.437
16.0	0.435	0.441
16.2	0.439	0.445
16.4	0.443	0.449
16.6	0.447	0.453
16.8	0.451	0.457

$I(s)$ and $I^b(s)$ curves of short nozzle-to-photofilm distance

s, Å^{-1}	$I(s)$	$I^b(s)$
7.0	0.342	0.383
7.2	0.338	0.378
7.4	0.333	0.373
7.6	0.333	0.368
7.8	0.336	0.363
8.0	0.341	0.359
8.2	0.347	0.354
8.4	0.351	0.349
8.6	0.353	0.345
8.8	0.353	0.341
9.0	0.350	0.337
9.2	0.345	0.333
9.4	0.338	0.329
9.6	0.333	0.326
9.8	0.330	0.322
10.0	0.327	0.319
10.2	0.324	0.316
10.4	0.321	0.312
10.6	0.316	0.309
10.8	0.310	0.306
11.0	0.303	0.303
11.2	0.296	0.300
11.4	0.290	0.298
11.6	0.284	0.295
11.8	0.279	0.292
12.0	0.275	0.289
12.2	0.272	0.287
12.4	0.271	0.284
12.6	0.272	0.282
12.8	0.275	0.280
13.0	0.279	0.277
13.2	0.283	0.275
13.4	0.286	0.273
13.6	0.287	0.272
13.8	0.285	0.270
14.0	0.280	0.268
14.2	0.275	0.266
14.4	0.269	0.265
14.6	0.264	0.263
14.8	0.260	0.261
15.0	0.257	0.260
15.2	0.255	0.258
15.4	0.253	0.257
15.6	0.252	0.255
15.8	0.251	0.254

16.0	0.249	0.252
16.2	0.247	0.251
16.4	0.246	0.250
16.6	0.244	0.249
16.8	0.243	0.247
17.0	0.242	0.246
17.2	0.241	0.245
17.4	0.241	0.244
17.6	0.242	0.243
17.8	0.243	0.243
18.0	0.245	0.242
18.2	0.247	0.241
18.4	0.247	0.240
18.6	0.247	0.240
18.8	0.246	0.239
19.0	0.243	0.238
19.2	0.240	0.237
19.4	0.237	0.237
19.6	0.235	0.236
19.8	0.232	0.235
20.0	0.231	0.235
20.2	0.230	0.234
20.4	0.230	0.234
20.6	0.231	0.233
20.8	0.231	0.233
21.0	0.231	0.232
21.2	0.231	0.232
21.4	0.231	0.231
21.6	0.231	0.231
21.8	0.230	0.231
22.0	0.230	0.230
22.2	0.230	0.230
22.4	0.230	0.230
22.6	0.230	0.230
22.8	0.230	0.229
23.0	0.230	0.229
23.2	0.230	0.229
23.4	0.230	0.229
23.6	0.230	0.228
23.8	0.230	0.228
24.0	0.230	0.228
24.2	0.229	0.228
24.4	0.228	0.228
24.6	0.227	0.228
24.8	0.227	0.228
25.0	0.227	0.228
25.2	0.227	0.228
25.4	0.227	0.228

25.6	0.227	0.228
25.8	0.228	0.229
26.0	0.228	0.229
26.2	0.229	0.229
26.4	0.230	0.230
26.6	0.230	0.230
26.8	0.231	0.230
27.0	0.231	0.231
27.2	0.231	0.231
27.4	0.232	0.231
27.6	0.232	0.232
27.8	0.232	0.232
28.0	0.233	0.233
28.2	0.233	0.233
28.4	0.234	0.234
28.6	0.235	0.235
28.8	0.236	0.235
29.0	0.236	0.236
29.2	0.237	0.237
29.4	0.238	0.238
29.6	0.238	0.238
29.8	0.239	0.239
30.0	0.240	0.240

Table S3. The corrections ($r_{ij,e} - r_{ij,a}$) to internuclear distances $r_{ij,a}$, theoretical $u_{ij,\mathrm{h1}}$ and experimental $u_{ij,\mathrm{exp}}$ root-mean-square vibrational amplitudes (Å) for PhDBH.

Atom pair distance		$r_{ij,a}$	u(exp)	u(calc)	correction
C8	H20	1.096	0.075	0.075	-0.0152
C11	H23	1.097	0.075	0.075	-0.0152
C10	H22	1.097	0.075	0.075	-0.0154
C9	H21	1.098	0.075	0.075	-0.0155
C12	H24	1.099	0.075	0.075	-0.0153
C3	H16	1.103	0.076	0.076	-0.0161
C6	H13	1.103	0.076	0.076	-0.0164
C4	H19	1.103	0.076	0.076	-0.0162
C2	H15	1.104	0.076	0.076	-0.0163
C3	H17	1.104	0.076	0.076	-0.0159
C2	H14	1.106	0.076	0.076	-0.0163
C4	H18	1.106	0.076	0.076	-0.0164
C9	C8	1.392	0.058	0.045	-0.0072
C10	C9	1.394	0.058	0.045	-0.0051
C11	C10	1.397	0.058	0.045	-0.0095
C7	C12	1.397	0.058	0.045	-0.0069
C12	C11	1.398	0.058	0.045	-0.0107
C7	C8	1.402	0.058	0.045	-0.0109
C6	N1	1.444	0.065	0.051	0.0003
C6	N5	1.459	0.065	0.051	-0.0149
C2	N1	1.475	0.065	0.052	-0.0047
C4	N5	1.477	0.065	0.052	-0.0066
C7	C6	1.493	0.062	0.048	-0.0172
N1	N5	1.509	0.071	0.058	-0.0034
C4	C3	1.543	0.066	0.052	-0.0127
C2	C3	1.549	0.066	0.052	-0.0194
H16	H17	1.705	0.122	0.122	-0.0172
H18	H19	1.786	0.122	0.122	-0.0188
H15	H14	1.788	0.122	0.122	-0.0205
H19	N5	2.076	0.104	0.104	-0.0065
H15	N1	2.085	0.104	0.104	-0.0154
H14	N1	2.111	0.107	0.107	-0.0092
H18	N5	2.120	0.107	0.107	-0.0187
C7	H20	2.141	0.098	0.098	-0.0146
C11	H24	2.142	0.098	0.098	-0.0153
C8	H21	2.144	0.098	0.098	-0.0128
C9	H22	2.149	0.098	0.098	-0.0115
C10	H21	2.162	0.098	0.098	-0.0113
C7	H24	2.162	0.098	0.098	-0.0134
C10	H23	2.162	0.098	0.098	-0.0143
C11	H22	2.165	0.098	0.098	-0.0155
C12	H23	2.165	0.098	0.098	-0.0158
C9	H20	2.173	0.098	0.098	-0.012
H13	N1	2.180	0.102	0.102	-0.0087
H13	H16	2.183	0.222	0.222	0.0006
C7	H13	2.187	0.102	0.102	-0.0261
H13	N5	2.189	0.102	0.102	-0.0175

C3	H19	2.191	0.107	0.107	-0.012
C4	H16	2.207	0.108	0.108	-0.0193
C4	H17	2.207	0.108	0.108	-0.0173
C2	H13	2.211	0.108	0.108	-0.0235
C3	H15	2.212	0.107	0.107	-0.0331
C2	H17	2.215	0.108	0.108	-0.0248
C3	H14	2.231	0.107	0.107	-0.0199
C3	H18	2.236	0.107	0.107	-0.0256
C3	N1	2.401	0.078	0.060	-0.0104
C12	C8	2.405	0.074	0.056	-0.0099
C3	N5	2.405	0.078	0.060	-0.0145
C12	C10	2.405	0.074	0.056	-0.0157
C6	C4	2.413	0.088	0.070	0.0078
H19	H17	2.413	0.175	0.175	-0.0055
C11	C9	2.414	0.074	0.056	-0.0091
C10	C8	2.417	0.074	0.056	-0.0084
C7	C9	2.420	0.074	0.056	-0.0155
C2	N5	2.424	0.079	0.061	-0.0096
C4	N1	2.427	0.079	0.061	-0.0128
C6	C2	2.429	0.088	0.070	-0.0086
H14	H16	2.430	0.177	0.177	-0.0132
C7	C11	2.436	0.073	0.055	-0.0125
H13	C1	2.439	0.172	0.154	0.0069
H18	H16	2.442	0.177	0.177	-0.0256
H15	H17	2.443	0.175	0.175	-0.0355
H24	H13	2.457	0.214	0.214	-0.0592
C2	C4	2.460	0.083	0.061	-0.0239
H24	H23	2.464	0.160	0.160	-0.0134
H22	H21	2.477	0.178	0.160	-0.01
H21	H20	2.492	0.160	0.160	-0.0097
H23	H22	2.500	0.160	0.160	-0.0137
C7	N1	2.509	0.072	0.072	-0.0086
C12	C6	2.510	0.085	0.067	-0.018
C8	C6	2.511	0.083	0.065	-0.0235
H13	C4	2.516	0.151	0.151	0.0272
C7	N5	2.526	0.090	0.072	-0.0248
H13	C2	2.555	0.151	0.151	-0.0117
H13	H18	2.631	0.243	0.243	0.0491
H20	N1	2.678	0.268	0.268	-0.0351
C12	H13	2.684	0.147	0.147	-0.0456
H13	H14	2.685	0.243	0.243	-0.0049
H20	C6	2.686	0.140	0.140	-0.0213
H20	N5	2.686	0.268	0.268	-0.0437
C6	C3	2.692	0.083	0.080	-0.0049
H24	C6	2.728	0.141	0.141	-0.0177
C12	C9	2.769	0.067	0.063	-0.0137
C6	H18	2.781	0.159	0.159	0.0169
C11	C8	2.796	0.067	0.063	-0.0085
C7	C10	2.802	0.066	0.063	-0.0161
C6	H14	2.804	0.159	0.159	-0.0058

H14	H17	2.823	0.155	0.155	-0.0295
H18	H17	2.826	0.155	0.155	-0.0326
C6	H16	2.859	0.177	0.177	-0.0131
C8	N1	2.984	0.151	0.147	-0.0287
C2	H19	2.988	0.157	0.157	-0.0256
C8	N5	2.996	0.151	0.147	-0.0414
C4	H15	3.000	0.157	0.157	-0.0371
H16	N1	3.001	0.139	0.139	-0.0145
H15	N5	3.004	0.142	0.142	-0.0071
H16	N5	3.020	0.139	0.139	-0.0334
H19	N1	3.021	0.142	0.142	-0.0244
H19	H16	3.048	0.129	0.129	-0.0162
H15	H16	3.064	0.129	0.129	-0.032
H15	H19	3.151	0.263	0.263	-0.0341
H18	N1	3.270	0.108	0.108	-0.0108
H14	N5	3.275	0.108	0.108	-0.015
H17	N5	3.311	0.104	0.104	-0.0109
H17	N1	3.316	0.104	0.104	-0.0152
C6	H19	3.326	0.102	0.102	-0.0039
C6	H15	3.336	0.102	0.102	-0.0141
C4	H14	3.373	0.101	0.101	-0.0214
C12	H20	3.380	0.094	0.094	-0.015
C2	H18	3.381	0.101	0.101	-0.0293
C10	H24	3.384	0.094	0.094	-0.0206
C8	H22	3.396	0.094	0.094	-0.0145
C8	H24	3.399	0.094	0.094	-0.0173
C12	H22	3.399	0.094	0.094	-0.0216
C7	H21	3.400	0.094	0.094	-0.021
C9	H23	3.403	0.094	0.094	-0.0143
C11	H21	3.404	0.094	0.094	-0.0158
C10	H20	3.413	0.094	0.094	-0.0133
C7	H23	3.420	0.094	0.094	-0.0178
C8	H13	3.435	0.100	0.100	-0.0174
H13	H17	3.508	0.174	0.174	-0.0001
H13	H19	3.583	0.159	0.159	0.0159
H13	H15	3.617	0.159	0.159	-0.018
C12	N1	3.691	0.148	0.115	0.0115
C12	N5	3.707	0.148	0.115	-0.0045
H20	H13	3.735	0.156	0.156	-0.004
C7	C4	3.740	0.112	0.079	-0.0052
C7	C2	3.750	0.112	0.079	-0.0156
C6	H17	3.775	0.104	0.104	-0.0098
C9	C6	3.784	0.098	0.066	-0.0263
C11	C6	3.798	0.099	0.067	-0.0236
C12	H21	3.857	0.095	0.095	-0.0199
C9	H24	3.858	0.095	0.095	-0.0196
C11	H20	3.883	0.095	0.095	-0.0142
C8	H23	3.884	0.095	0.095	-0.0143
C7	H22	3.889	0.094	0.094	-0.022
C7	H18	3.938	0.177	0.177	0.0101

C7	H14	3.957	0.177	0.177	-0.0091
H24	N1	3.988	0.196	0.196	0.0225
H24	N5	4.004	0.196	0.196	0.0072
H14	H19	4.024	0.162	0.162	-0.027
H15	H18	4.041	0.162	0.162	-0.0441
C11	H13	4.070	0.146	0.146	-0.0462
H20	C2	4.120	0.275	0.275	-0.0156
H20	C4	4.136	0.275	0.275	-0.0317
H14	H18	4.142	0.157	0.157	-0.0197
C7	C3	4.180	0.113	0.085	-0.0169
C7	H16	4.269	0.192	0.192	-0.0234
H24	H20	4.284	0.129	0.129	-0.0206
H24	H22	4.288	0.129	0.129	-0.0241
C10	C6	4.288	0.097	0.069	-0.0266
H22	H20	4.305	0.129	0.129	-0.0169
H23	H21	4.305	0.129	0.129	-0.0187
C9	N1	4.331	0.166	0.138	-0.0242
C9	N5	4.343	0.166	0.138	-0.0364
C8	C2	4.414	0.177	0.149	-0.0198
C8	C4	4.419	0.177	0.149	-0.0243
H24	H16	4.449	0.298	0.298	-0.0395
H20	H15	4.493	0.336	0.336	-0.0301
H20	H19	4.525	0.336	0.336	-0.0615
H24	H18	4.529	0.419	0.419	0.0678
C7	H19	4.561	0.116	0.116	-0.0157
C7	H15	4.563	0.116	0.116	-0.0171
H24	H14	4.579	0.419	0.419	0.0182
C9	H13	4.588	0.110	0.110	-0.0246
H20	H14	4.600	0.366	0.366	0.0198
H20	H18	4.615	0.366	0.366	0.0046
H21	C6	4.647	0.110	0.110	-0.029
C12	H18	4.667	0.287	0.287	0.0375
H23	C6	4.667	0.111	0.111	-0.0264
C12	C4	4.702	0.353	0.152	0.0174
C12	H14	4.702	0.287	0.287	0.0018
H24	C4	4.703	0.259	0.259	0.0351
C12	C2	4.723	0.353	0.152	-0.0038
H24	C2	4.734	0.259	0.259	0.0042
C8	H18	4.738	0.231	0.231	-0.002
C8	H14	4.738	0.231	0.231	-0.002
H23	H13	4.755	0.187	0.187	-0.0546
H20	C3	4.828	0.189	0.189	-0.0262
C12	H16	4.843	0.234	0.234	-0.0313
C10	H13	4.844	0.130	0.130	-0.0371
H24	C3	4.848	0.220	0.220	-0.009
C11	N1	4.858	0.320	0.118	0.0057
C11	N5	4.873	0.320	0.118	-0.0097
H24	H21	4.944	0.118	0.118	-0.0241
H23	H20	4.968	0.118	0.118	-0.0183
H21	N1	4.985	0.196	0.196	-0.0327

C8	H15	4.988	0.203	0.203	-0.0265
H21	N5	4.995	0.196	0.196	-0.0427
C8	H19	5.006	0.203	0.203	-0.0439
C12	C3	5.025	0.213	0.131	-0.0113
C8	C3	5.039	0.182	0.100	-0.0238
C10	N1	5.109	0.199	0.117	-0.0092
C10	N5	5.123	0.199	0.117	-0.0231
C7	H17	5.261	0.108	0.108	-0.0203
H20	H16	5.335	0.225	0.225	-0.0124
C8	H16	5.346	0.183	0.183	-0.0202
H22	C6	5.374	0.099	0.099	-0.0306
H21	H13	5.532	0.134	0.134	-0.0212
C12	H19	5.626	0.168	0.168	0.0182
C12	H15	5.640	0.168	0.168	0.0043
H24	H19	5.718	0.267	0.267	0.042
C9	C2	5.743	0.224	0.142	-0.0161
H24	H15	5.744	0.267	0.267	0.0158
C9	C4	5.746	0.224	0.142	-0.0189
H20	H17	5.757	0.218	0.218	-0.03
H23	N1	5.786	0.161	0.161	0.0106
H23	N5	5.801	0.161	0.161	-0.0047
H24	H17	5.895	0.245	0.245	-0.0098
H22	H13	5.913	0.152	0.152	-0.0407
C11	H18	5.920	0.285	0.285	0.0305
C11	H14	5.951	0.285	0.285	-0.0006
C9	H18	5.966	0.228	0.228	0.0009
C9	H14	5.969	0.228	0.228	-0.0022
C11	C4	5.978	0.230	0.148	0.0125
C11	C2	5.995	0.230	0.148	-0.0047
C8	H17	6.061	0.129	0.129	-0.0265
C12	H17	6.111	0.153	0.153	-0.0126
H22	N1	6.162	0.146	0.146	-0.0116
H22	N5	6.175	0.146	0.146	-0.0251
C11	H16	6.231	0.235	0.235	-0.032
C9	H15	6.307	0.204	0.204	-0.0173
C9	H19	6.324	0.204	0.204	-0.0343
C9	C3	6.386	0.178	0.123	-0.0203
C11	C3	6.387	0.205	0.096	-0.0126
C10	C4	6.414	0.205	0.123	-0.0035
H21	C2	6.418	0.210	0.210	-0.0162
C10	C2	6.421	0.205	0.123	-0.0104
H21	C4	6.428	0.210	0.210	-0.0257
C10	H18	6.476	0.229	0.229	0.0127
C10	H14	6.493	0.229	0.229	-0.0043
C9	H16	6.620	0.189	0.189	-0.0206
H23	H18	6.635	0.365	0.365	0.0424
H23	H14	6.673	0.365	0.365	0.0039
H21	H14	6.700	0.293	0.293	0.0042
H21	H18	6.706	0.293	0.293	-0.0017
H23	C4	6.795	0.210	0.210	0.0213

H23	C2	6.817	0.210	0.210	-0.0007
C11	H19	6.837	0.174	0.174	0.0149
C11	H15	6.845	0.174	0.174	0.0067
H21	H15	6.847	0.282	0.282	-0.0194
H23	H16	6.854	0.277	0.277	-0.0367
H21	H19	6.873	0.282	0.282	-0.0455
C10	C3	6.964	0.098	0.098	-0.0159
C10	H16	6.999	0.211	0.211	-0.0266
C10	H15	7.126	0.170	0.170	-0.0035
C10	H19	7.131	0.170	0.170	-0.0085
H21	C3	7.135	0.147	0.147	-0.0212
H23	C3	7.137	0.176	0.176	-0.011
C9	H17	7.421	0.124	0.124	-0.0209
C11	H17	7.473	0.144	0.144	-0.0118
H22	C4	7.473	0.153	0.153	-0.0039
H21	H16	7.474	0.205	0.205	-0.0167
H22	C2	7.480	0.153	0.153	-0.0102
H22	H18	7.509	0.258	0.258	0.0126
H22	H14	7.526	0.258	0.258	-0.0039
H23	H19	7.700	0.231	0.231	0.0304
H23	H15	7.715	0.231	0.231	0.0159
C10	H17	8.041	0.118	0.118	-0.0151
H22	C3	8.046	0.122	0.122	-0.016
H22	H16	8.072	0.226	0.226	-0.0275
H21	H17	8.126	0.179	0.179	-0.0208
H22	H15	8.157	0.201	0.201	-0.0011
H22	H19	8.164	0.201	0.201	-0.0075
H23	H17	8.210	0.199	0.199	-0.0084
H22	H17	9.120	0.139	0.139	-0.0136

Table S4. Computed relative energies (in kJ/mol) of the possible conformers of PhDBH and the transition state related to the interconversion between the boat and *exo*-chair conformers.

Structure	Symmetry group	ΔE_e [a]	ΔE_0 [b]	ΔE_0 [c]	ΔG_{363} [d]
Boat	C_s	0.0	0.0	0.0	0.0
exo-chair	C_s	15.7	11.9	14.3	12.1
endo-chair	C_s	50.6	52.2	45.8	54.4
TS $_{\text{boat}\rightarrow exo\text{-chair}}$	C_s	16.0	12.8	17.6	14.6

[a] B3PW91/6-31G(d,p). [b] B3LYP/cc-pVTZ. [c] MP2/cc-pVTZ. [d] B3LYP/6-31+G(d,p)(PCM) [Reference S2].

Table S5. Cartesian coordinates of molecular structure of PhDBH boat conformer (GED, Å).

N	1.42718890	0.60864670	-0.75300000
C	2.70217670	0.04392590	-1.21840880
C	3.31736490	-0.64657810	0.00000000
C	2.70217670	0.04392590	1.21840880
N	1.42718890	0.60864670	0.75300000
C	0.64708410	-0.34548650	0.00000000
C	-0.82033210	-0.18782560	0.00000000
C	-1.39050680	1.08099160	0.00000000
C	-2.76845200	1.22101650	0.00000000
C	-3.59122750	0.10187540	0.00000000
C	-3.03643960	-1.16938170	0.00000000
C	-1.65542940	-1.29859080	0.00000000
H	0.98223530	-1.37910790	0.00000000
H	2.51870580	-0.62164850	-2.06101730
H	3.31470880	0.87486520	-1.55976220
H	3.14133220	-1.71889530	0.00000000
H	4.40407550	-0.60019420	0.00000000
H	2.51870580	-0.62164850	2.06101730
H	3.31470880	0.87486520	1.55976220
H	-0.72922180	1.93613090	0.00000000
H	-3.19512440	2.21533770	0.00000000
H	-4.66458070	0.23428930	0.00000000
H	-3.67111110	-2.04506010	0.00000000
H	-1.23390940	-2.29662710	0.00000000

Table S6. Selected geometric parameters of BH and DBH moieties in compounds **1**–**7**.

	MW		GED				
Parameter	BH **1**[a]	Sabinene **7**[b]	DBH **2**[c]	6-MDBH **3**[d]	6,6-DMDBH **4**[e]	PhDBH **5**[f]	6,6′-BDBH **6**[g]
	Bond distances/Å						
	r_0	r_s	r_e				r_g
r(N–N)			1.506(13)	1.512(2)	1.522(7)	1.506	1.511(2)
r(C_{diaz}–N)			1.442(2)	1.440(2)	1.444(7)	1.444(21)	1.452(2)
r(C_{cycl}–C_{cycl})	1.530	1.541(2)	1.524(7)	1.523(2)	1.541(7)	1.530(12)	1.543(2)
r(C_{diaz}–C_{Ph})				1.487(2)		1.476(12)	
r(C_{cycl}–N)			1.469 (4)	1.466(2)	1.472(7)	1.470(24)	1.483(2)
	Bond angles/deg						
C–C(H_2)–C	107.9	104.3(2)	104.0 (10)	99.9(4)	102.3(28)	105.6(38)	102.8
N–C–N			63.0	63.3(1)	63.2	62.8(9)	62.9
N–N–C_{diaz}			107.7(4)	106.1(2)	107.6(9)	108.5(14)	107.5
N–C_{diaz}–C_{Ph}				114.9(6)		117.8(16)	
	Out-of-plane angles/deg						
α	38.0	26.5(9)	26.5(19)	26.2(3)	1.2 (30)	24.4	
β	63.0	70.6(5)	71.3(9)	74.0(1)	72.0(12)	74.6	

[a] References S4 and S5. [b] Reference S4. [c] Reference S6. [d] Reference S7. [e] Reference S8. [f] This work. [g] Reference S9.

Table S7. Characteristics of crystalline 1,5-diazabicyclo[3.1.0]hexane derivatives.

	Space group	Z	Density ρ, g/cm^3	Lattice constant a, A^{-1}	Lattice constant b, A^{-1}	Lattice constant c, A^{-1}
6-phenyl-1,5-diazabicyclo[3.1.0]hexane [a]	*P*na2_1	4	1.207 (T=293K)	8.845	8.798	11.327
6-(4-bromophenyl)-1,5-diazabicyclo[3.1.0]hexane [b]	*P*$2_12_12_1$	8	1.613 (T=296K)	5.5775	7.701	22.926
6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane [a]	*Pbca*	8	1.240 (T=293K)	8.450	9.236	26.103
6-(4-chlorophenyl)-1,5-diazabicyclo[3.1.0]hexane [c]	*Pbca*	8	1.374 (T=110 K)	14.255	8.935	14.779
6,6'-dimethyl-1,1',5,5'-tetraaza-6,6'-bi(bicyclo[3.1.0]hexane) [d]	*P2₁/c*	4	1.305 (T=120 K)	5.506	9.450	9.512
6-(4-nitrophenyl)-3,3-dimethyl-1,5-diazabicyclo[3.1.0]hexane [b]	*P2₁/c*	4	1.274 (T=296K)	6.489	11.518	16.471
6-(4-chlorophenyl)-3,3-dimethyl-1,5-diazabicyclo[3.1.0]hexane [b]	*P*2_1	4	1.262 (T=120K)	6.106	16.401	11.774
6-(4-fluorophenyl)-3,3-dimethyl-1,5-diazabicyclo[3.1.0]hexane [b]	*P2₁/c*	4	1.222 (T=296K)	12.583	9.542	9.720

[a] Reference S10. [b] Reference S11. [c] Reference S12. [d] Reference S13.

Table S8. Coefficients of linear regression of Eq.(1) (α_1, β_1 (g/(cm^3·[kcal/mol]^2)), γ_1 (g/cm^3)) taken from literature and the resulting molecular crystal density of PhDBH.

Calculation level	Eq.(1) fitted by Politzer			Eq.(1) fitted by Rice			$\rho = \left(\frac{M}{V_m}\right)$
	α_1	β_1	γ_1	α_1	β_1	γ_1	
B3PW91/6-31G(d,p)	0.9183[a]	0.0028[a]	0.0443[a]				
B3LYP/6-31G(d,p)				1.0462[b]; 1.0266[c]	0.0021[b]; 0.000543[c]	-0.1586[b]; -0.07027[c]	
Molecular crystal density of PhDBH							
B3PW91/6-31G(d,p)	1.242 [a]			1.187 [b]; 1.225 [c]			1.253
B3LYP/6-31G(d,p)	1.230 [a]			1.175 [b]; 1.215 [c]			1.243
B3LYP/6-311++G(3df,p)	1.210 [a]			1.150 [b]; 1.188 [c]			1.217
B3LYP/cc-pVTZ	1.220 [a]			1.163 [b]; 1.202 [c]			1.230
MP2/cc-pVTZ	1.224 [a]			1.166 [b]; 1.203 [c]			1.231

[a] Parameterization based on a set of 37 substances. [b] Parameterization based on a data set of 180 CHNO compounds. [c] Parameterization based on a selected set of 113 CHNO compounds, for which deviation of the calculated (at the B3LYP/6-31G(d,p) level) and experimental crystal densities was less than 0.050 g/cm^3.

Molecular electrostatic potentials were computed on the 0.001 a.u. molecular surfaces and then the descriptors of resulting surface potentials $V_S(r)$ were analyzed:

- total variance σ_{tot}^2 of surface potential $V_S(r)$:

  $\sigma_{tot}^2 = \sigma_+^2 + \sigma_-^2 = \frac{1}{r}\sum_{i=1}^{r}[V_S^+(r_i) - \bar{V}_S^+]^2 + \frac{1}{s}\sum_{j=1}^{s}[V_S^-(r_j) - \bar{V}_S^-]^2$, where $\bar{V}_S^+$ and $\bar{V}_S^-$ are positive and negative averages.

- electrostatic balance between the positive and negative potentials on a molecular surface, ν:

$$\nu = \frac{\sigma_+^2\sigma_-^2}{\sigma_{tot}^2}$$

Table S9. The C_{Ph}-C_{Ph}-C-H dihedral angles (deg.) in PhBDH molecules in the $(PhDBH)_n$ clusters of different size

Cluster	$(PhDBH)_3$	$(PhDBH)_4$	$(PhDBH)_5$	$(PhDBH)_6$	$(PhDBH)_7$
C_{Ph}-C_{Ph}-C-H	0.9, –6.4, –8.3	1.2, –3.9, –4.6, –18.4	8.7, –5.0, –11.8, –1.9, –1.5	6.1, –3.2, –0.7, –1.7, 6.2, –6.1	16.2, –14.9, 7.1, –3.6, –2.6, 1.7, 0.4

Table S10. Adiabatic (DE_{ad})[a] and vertical (DE_v)[b] dissociation energies (in kcal/mol) of the optimized $(PhDBH)_n$ clusters according to the DFT-B3LYP/6-31G(d,p) calculations

Cluster	$(PhDBH)_2$	$(PhDBH)_3$	$(PhDBH)_4$	$(PhDBH)_5$	$(PhDBH)_6$	$(PhDBH)_7$
DE_{ad}	0.6	1.4	3.9	3.9	6.1	7.5
DE_v	0.7	1.6	4.4	4.3	6.7	8.2

[a] $DE_{\mathrm{ad}} = nE(\mathrm{PhDBH}) - E[(\mathrm{PhDBH})_n] - \mathrm{BSSE}$. [b] $DE_{\mathrm{v}} = \sum_{\mathrm{k}=1}^{\mathrm{i}} E'_{\mathrm{k}}(\mathrm{PhDBH}) - E[(\mathrm{PhDBH})_n] - \mathrm{BSSE}$.

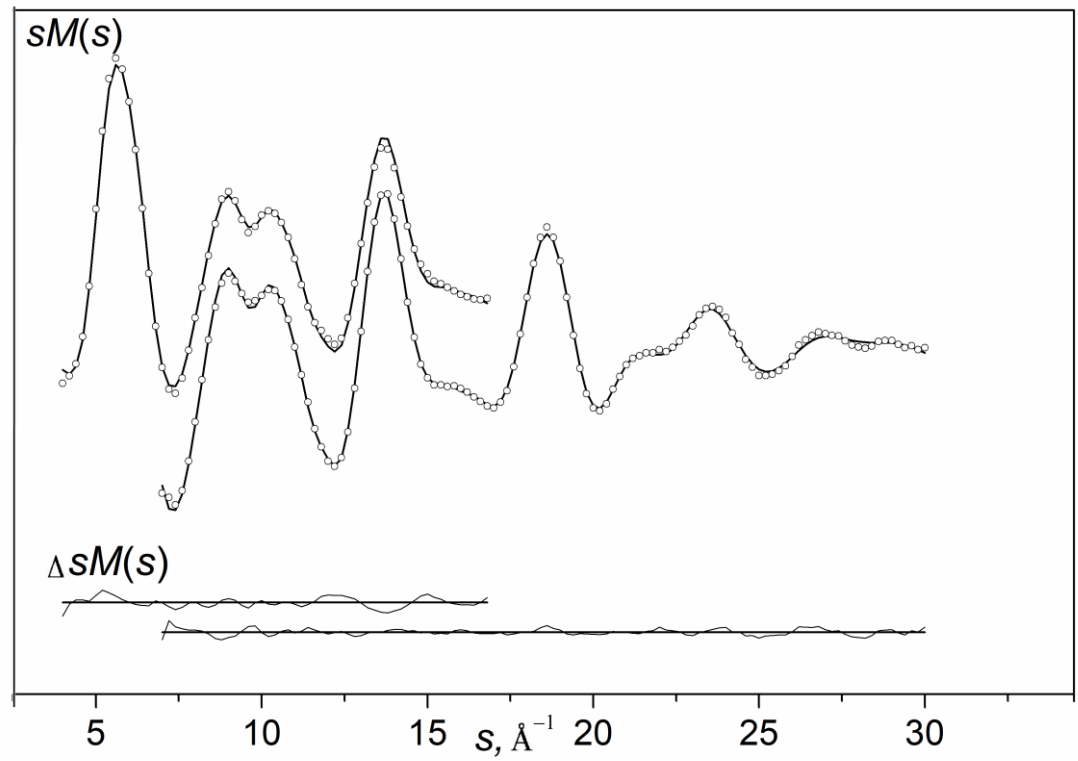


Figure S1. The molecular GED intensities *sM*(*s*) of PhDBH

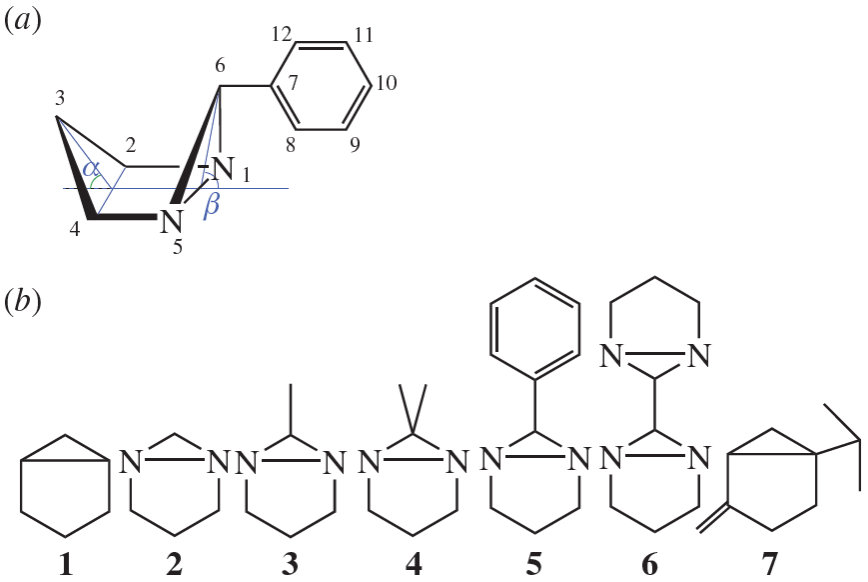


Figure S2 (*a*) Out-of-plane angles α and β in the PhDBH molecule, defined relative to the midpoints of the C2···C4 and N1–N5 distances, respectively. (*b*) A set of DBHs **2**–**6** and related compounds **1** and **7** for which semi-experimental structures have been determined by GED or MW spectroscopy: bicyclo[3.1.0]hexane (BH) **1**,[S4,S5] 1,5-diazabicyclo[3.1.0]hexane (DBH) **2**,[S6] 6-methyl-1,5-diazabicyclo[3.1.0]hexane (6-MDBH) **3**,[S7] 6,6-dimethyl-1,5-diazabicyclo[3.1.0]hexane (6,6-DMDBH) **4**,[S8] PhDBH **5**, 6,6′-bis(1,5-diazabicyclo[3.1.0]hexane) (6,6′-BDBH) **6**[S9] and sabinene [4-methylene-1-(1-methylethyl)bicyclo[3.1.0]hexane] **7**.[S4]

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