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Enthalpy of formation of 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane: determination by experimental and computational methods

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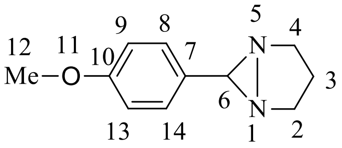
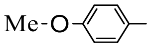
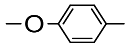
S1. Synthetic procedure

Bu^{t}OCl (7.4 ml, 70 mmol) was added dropwise to a solution of propane-1,3-diamine (13.0 ml, 155 mmol) in MeOH (100 ml) with vigorous stirring at –5 to 0 °C, followed by the addition of 4-methoxybenzaldehyde (8.5 ml, 70 mmol). The reaction mixture was kept at 0–5 °C for 24 h. The precipitate was filtered off, the solvent was evaporated *in vacuo*, and $CHCl_3$ (50 ml) was added to the residue. The precipitate was filtered off, the solution was washed with water (50 ml), dried over K_2CO_3, and the solvent was evaporated *in vacuo*. The residue was crystallized from diethyl ether to yield 6.1 g (45.9%) of 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane.

S2. Identification of 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane

S2.1. General remarks. All starting materials were purchased from commercial sources. NMR spectra were recorded on Bruker Avance 600 spectrometers at room temperature; the chemical shifts δ were measured in ppm relative to solvent ($CDCl_3$, ^1H NMR δ: 7.26, ^{13}C NMR δ: 77.0). Splitting patterns are indicated as s (singlet) and m (multiplet). Coupling constants (J) are given in Hz. The structures of the synthesized compounds were elucidated by 1D NMR (^1H, ^{13}C) and 2D NMR (^1H–^{13}C HSQC and HMBC, ^1H–^1H NOESY) spectroscopy. IR spectra were recorded on Bruker 'Alpha' spectrometers in the range 400–4000 cm^{-1} (resolution 2 cm^{-1}). High-resolution mass spectra were recorded on a Bruker micro TOF-QTM spectrometer with electrospray ionization (ESI). All measurements were performed in positive (+MS) ion mode (interface capillary voltage: 4500 V) with a scan range of m/z: 50–3000. External calibration of the mass spectrometer was performed with Electrospray Calibrant Solution (Fluka). Direct syringe injection was used for all analyzed solutions in MeCN (flow rate: 3 μl min^{-1}). Mass spectra were also measured on a Finnigan MAT INCOS-50 instrument. Melting points (mp) were determined using Electrothermal 9100 and SMP-20 capillary melting point instruments; the mp obtained in this work is 98−99 °C (94−95 °C,[S1] 98−99 °C[S2]).



S2.2. *6-(4-Methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane*. ^{1}H NMR (600.13 MHz, $CDCl_3$) δ: 1.82–1.92 (m, 2H, H-3), 3.06 (s, 1H, H-6), 3.09–3.14 (m, 2H, H-2a, H-4a), 3.53–3.57 (m, 2H, H-2b, H-4b), 3.77 (s, 3H, Me), 6.84–6.86 (d, 2H, H-9, H-13, $^3J_{H\text{-}9,H\text{-}8}$ 8.7 Hz, $^3J_{H\text{-}13,H\text{-}14}$ 8.7 Hz), 7.24–7.27 (d, 2H, H-8, H-14). ^{13}C NMR (150.90 MHz, $CDCl_3$) δ: = 21.63 (C^3), 52.06 (C^2), (C^4), 55.18 (C^{12}), 56.21 (C^6), 113.67 (C^9), (C^{13}), 128.27 (C^8), (C^{14}), 129.08 (C^7), 159.81 (C^{10}). IR (KBr, ν/cm^{-1}): 3079, 3049, 3010, 2979, 2937, 2872, 2847, 1611, 1585, 1518, 1472, 1455, 1445, 1431, 1403, 1388, 1368, 1302, 1252, 1228, 1185, 1171, 1156, 1106, 1025, 970, 912, 877, 865, 828, 809, 769, 718, 701, 644, 571, 538. HRMS (ESI-TOF), *m*/*z*: 191.1182 $[M+H]^+$ (calc. for $C_{11}H_{15}N_2O^+$, *m*/*z*: 191.1179). MS (EI, 70 eV), *m*/*z* (%): 191 ($[M+H]^+$, 3), 190 (M^+, 31), 189 ($[M-H]^+$, 100), 175 ($[M-Me]^+$, 2), 161 ($[M-Me-CH_2]^+$, 24), 148 ($[M-3CH_2]^+$, 3), 147 ($[M-Me-2CH_2]^+$, 5), 134 ($[M-Me-3CH_2+H]^+$, 19), 133 ($[M-Me-3CH_2]^+$, 5), 107 ([]$^+$, 5), 92 ([]$^+$, 7), 77 (Ph^+, 15).

S2.3. Copies of NMR spectra.

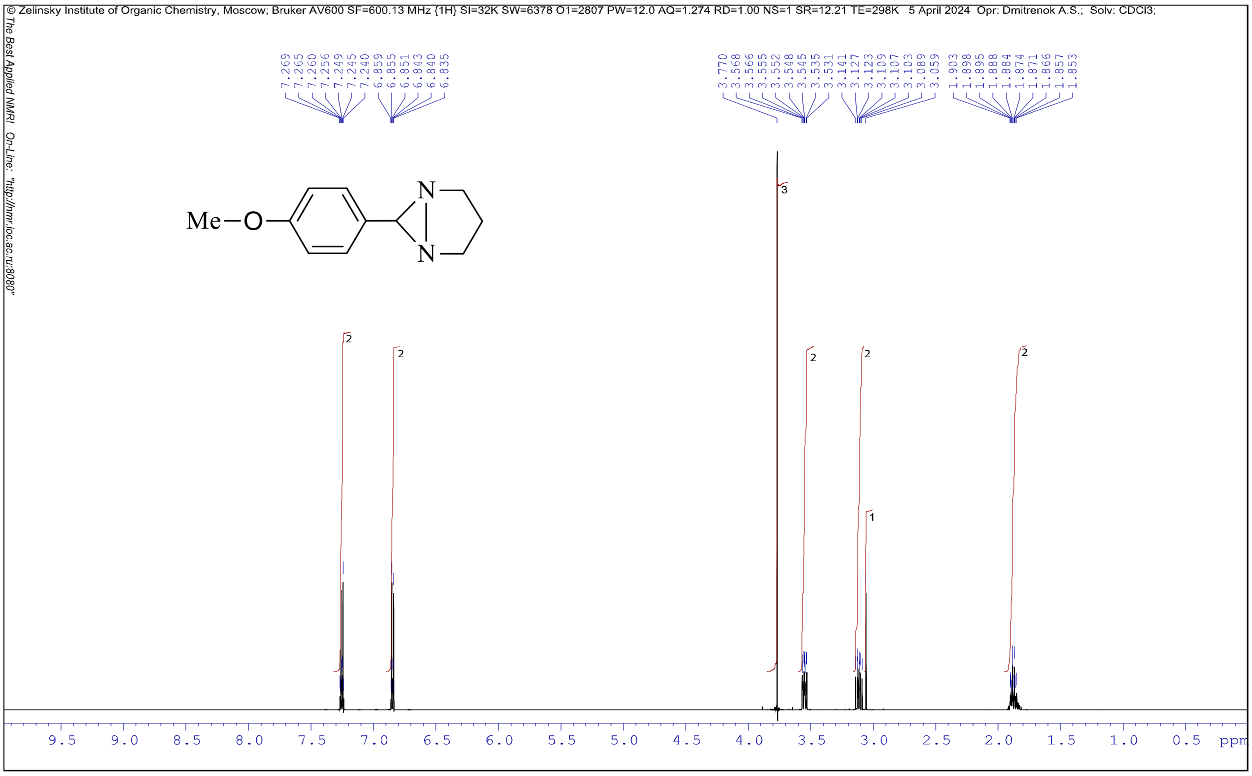


Figure S1 ^{1}H NMR spectrum of 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane ($CDCl_3$).

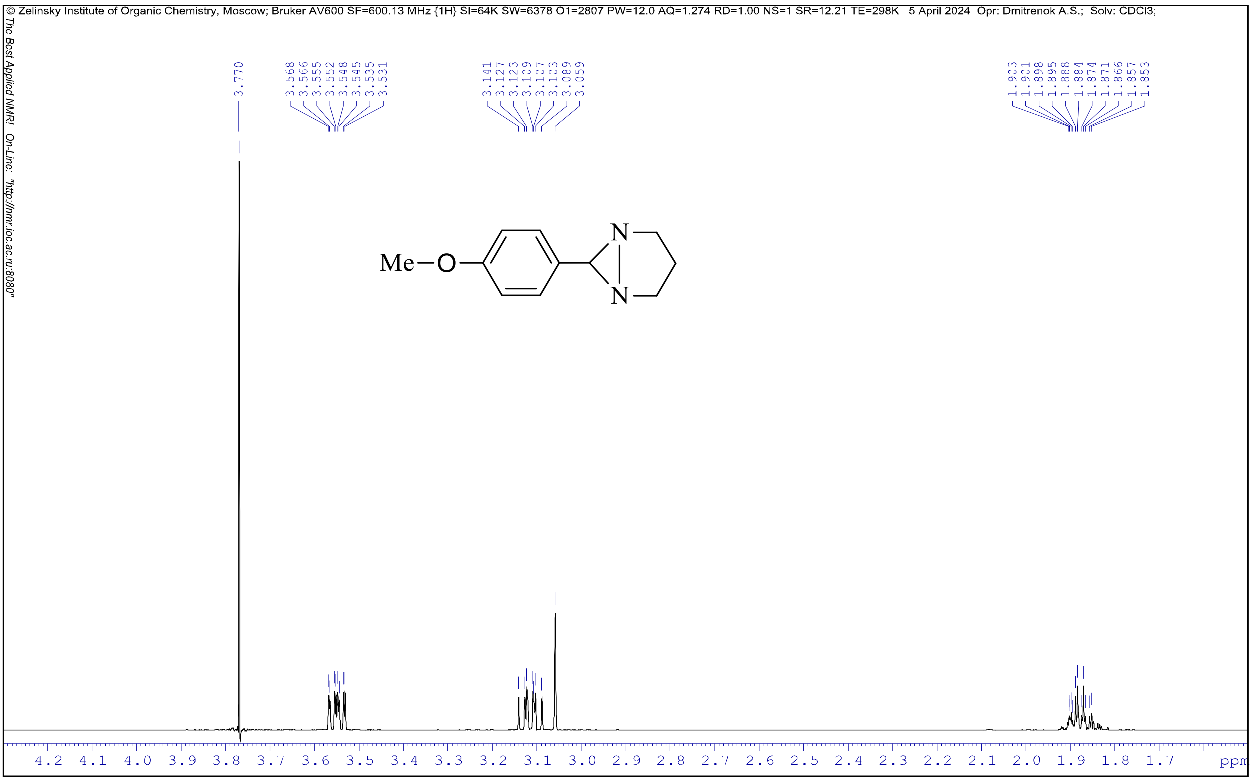


Figure S2 Fragment 1 of the ^{1}H NMR spectrum of 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane (CDCl$_3$).

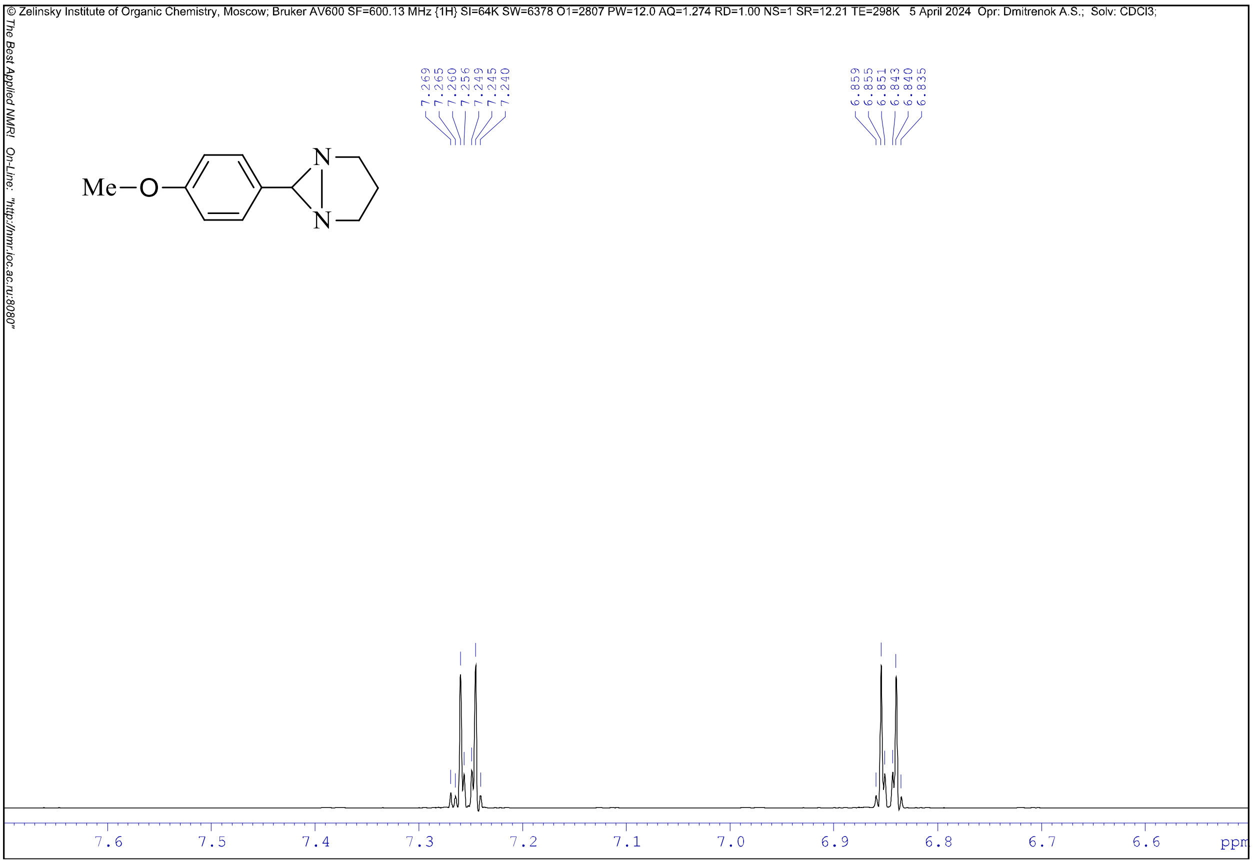


Figure S3 Fragment 2 of the ^{1}H NMR spectrum of 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane (CDCl$_3$).

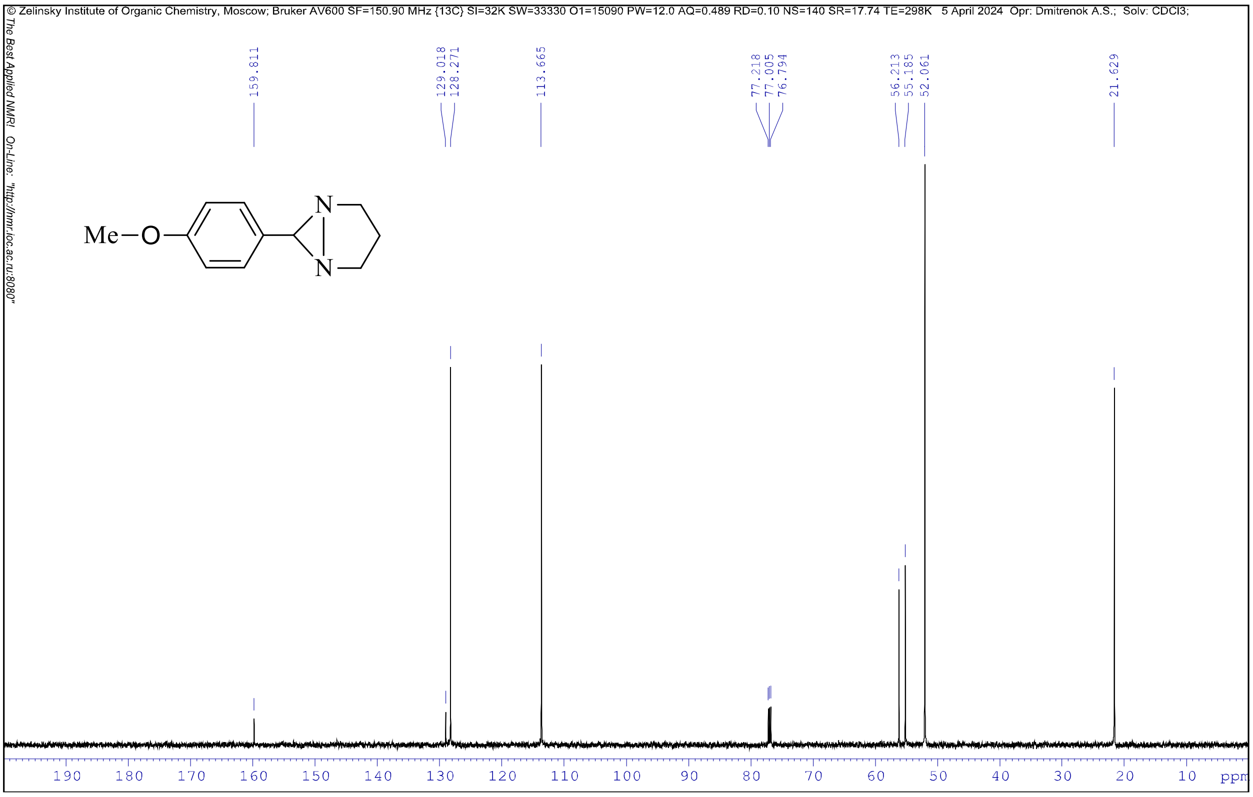


Figure S4 ^{13}C NMR spectrum of 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane ($CDCl_3$).

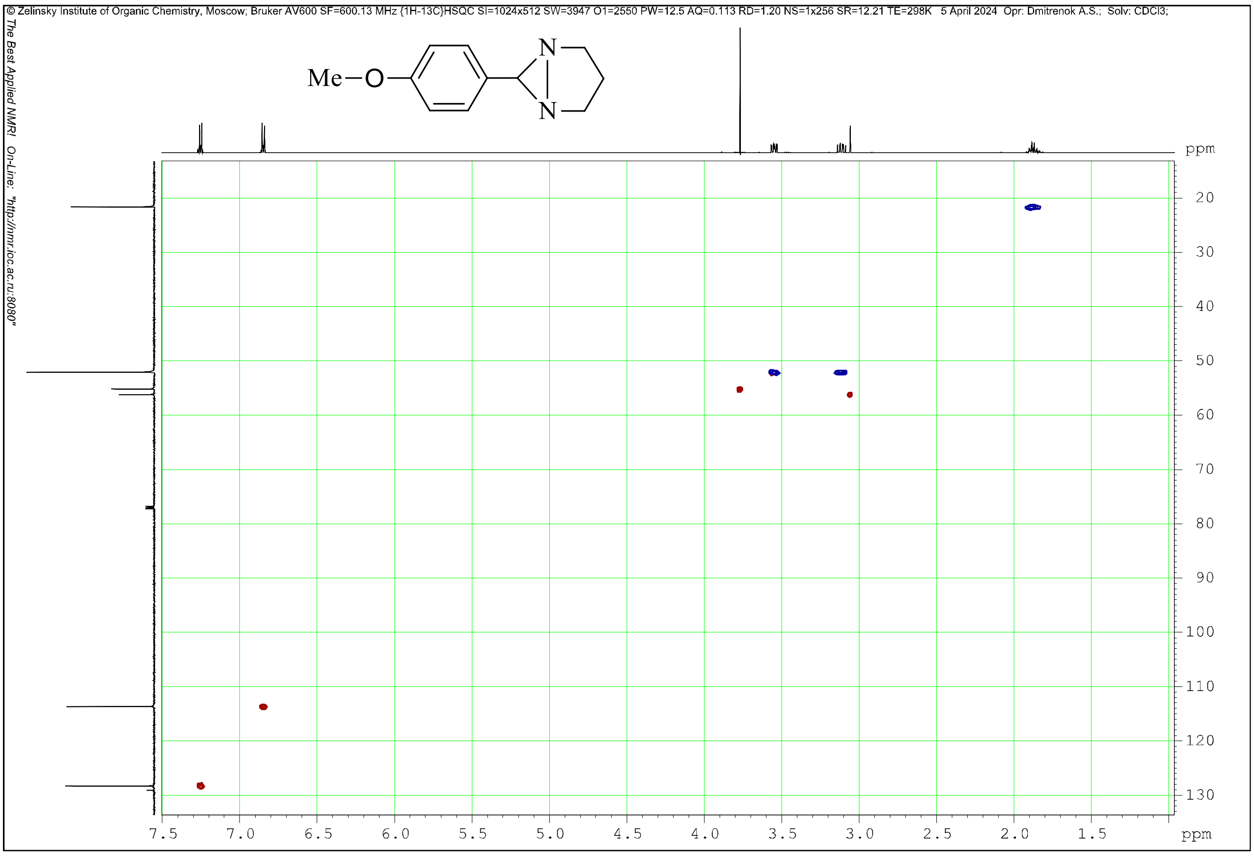


Figure S5 {^{1}H–^{13}C} HSQC spectrum of 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane ($CDCl_3$).

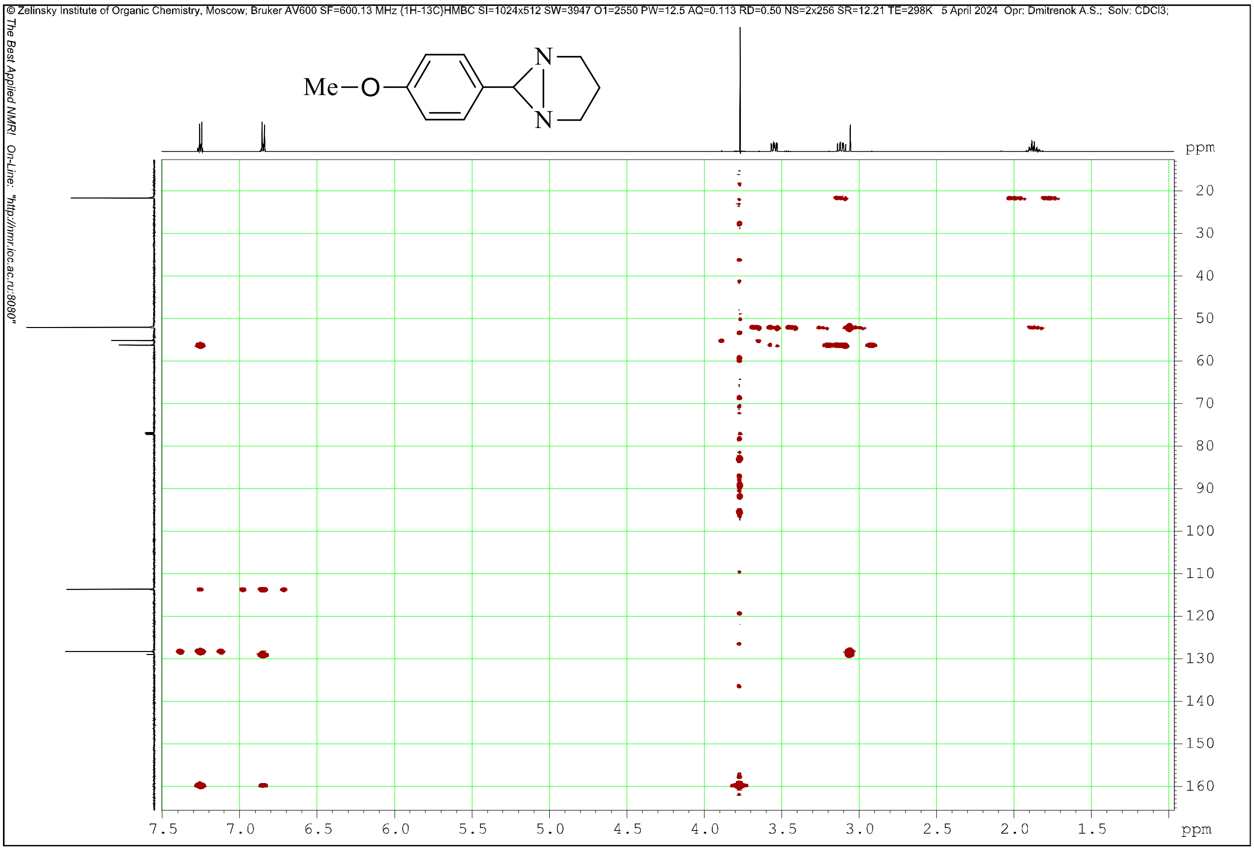


Figure S6 {^{1}H–^{13}C} HMBC spectrum of 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane (CDCl$_3$).

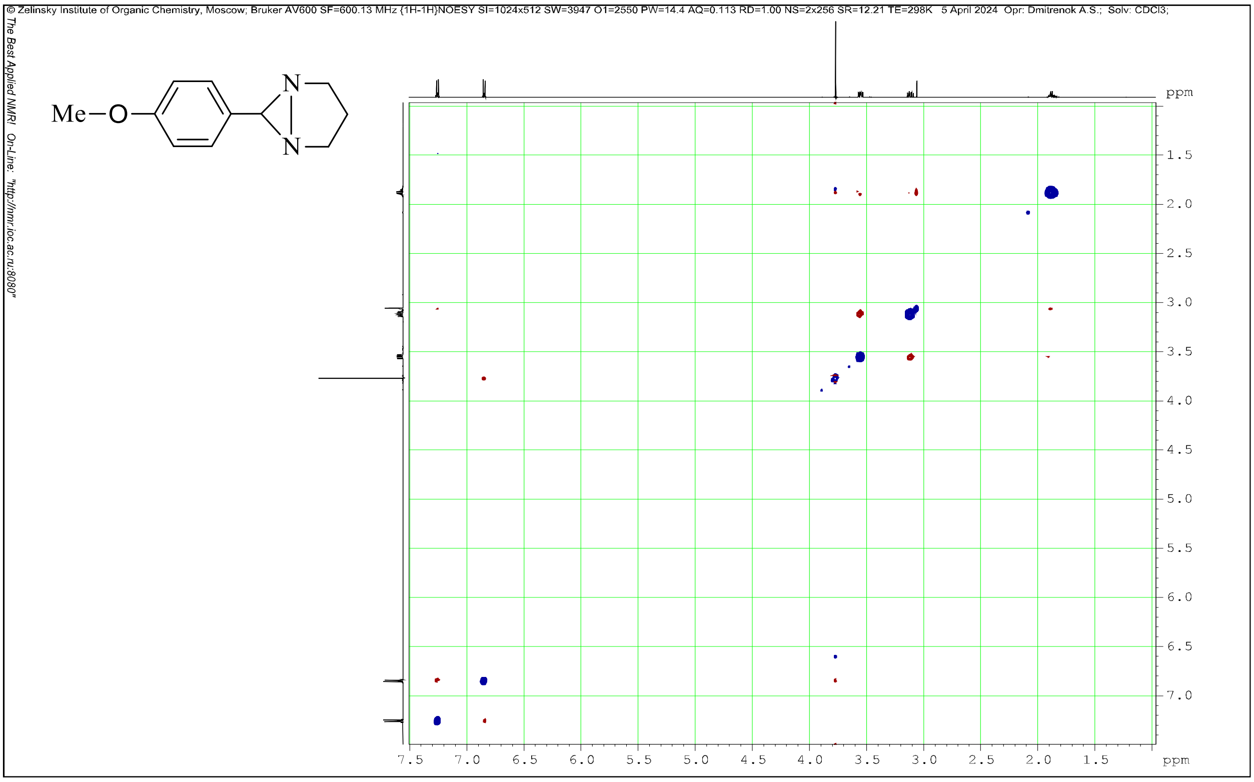


Figure S7 {^{1}H–^{1}H} gNOESY spectrum of 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane (CDCl$_3$).

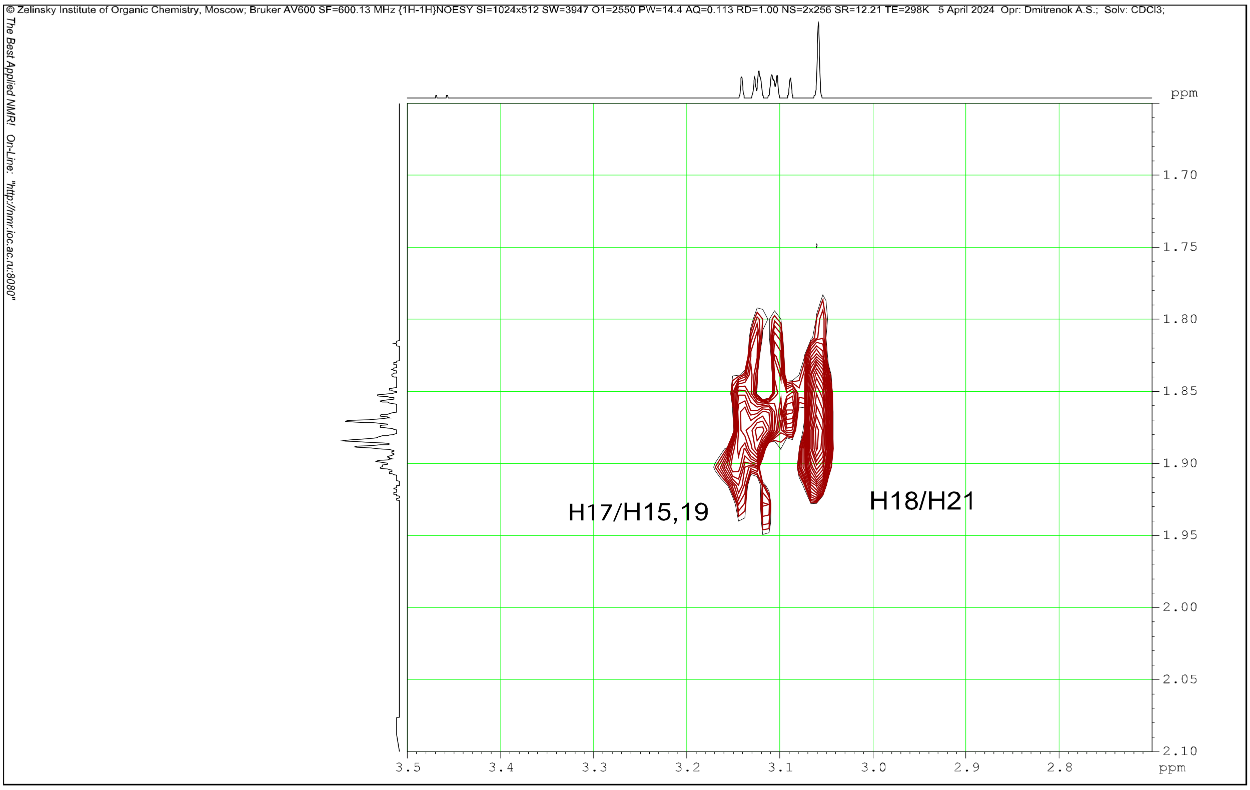


Figure S8 Fragment of the {^{1}H–^{1}H} gNOESY spectrum of 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane ($CDCl_3$). Atom numbering is given in Figure S10. Proton H18 has cross-peaks with proton H21. Proton H17 has cross-peaks with protons H15 and H19.

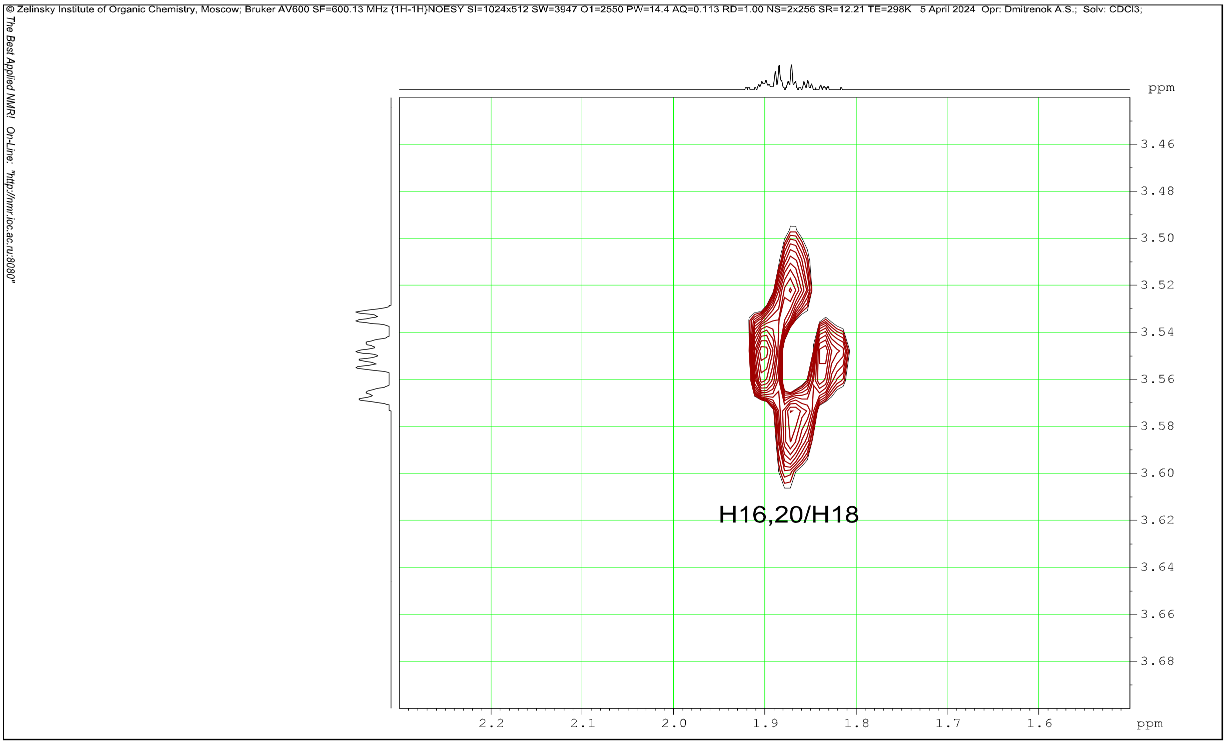


Figure S9 Fragment of the {^{1}H–^{1}H} gNOESY spectrum of 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane ($CDCl_3$). Atom numbering is given in Figure S10. Proton H18 has cross-peaks with protons H16 and H20.

S3. The data of the 2D NMR spectra.

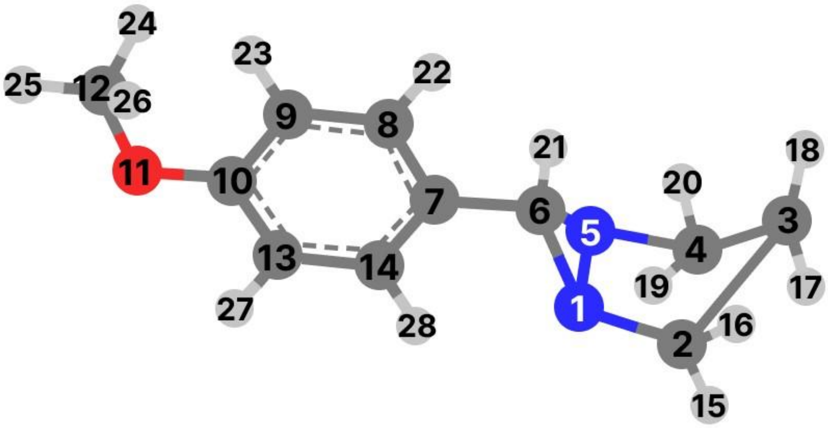


Figure S10. Numbering of atoms in the 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane molecule.

Table S1. The {^{1}H–^{13}C} HSQC, and {^{1}H–^{13}C} HMBC data for 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane (Figures S5 and S6). Atom numbering is given in Figure S10.

No. of atom	^{13}C NMR δ/ppm	{^{1}H-^{13}C} HSQC interactions	{^{1}H-^{13}CHMBC interactions
C2	52.06	H15, H16	H17, H18, H19, H20, H21
C3	21.63	H17, H18	H15, H16, H19, H20
C4	52.06	H19, H20	H15, H16, H17, H18, H21
C6	56.21	H21	H15, H16, H19, H20, H22, H28
C7	129.08	–	H21, H22, H23, H27, H28
C8	113.67	H22	H21, H23, H28
C9	128.27	H23	H22, H27
C10	159.81	–	H22, H23, H24, H25, H26, H27, H28
C12	55.18	H24, H25, H26	–
C13	128.27	H27	H23, H28
C14	113.67	H28	H21, H22, H27

Table S2. Partial {^{1}H–^{1}H} gNOESY data for 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane (Figures S7 and S8). Atom numbering is given in Figure S10.

No. of atom	^{1}H NMR δ/ppm	{^{1}H–^{1}H} gNOESY interactions
H15	3.09–3.14, m	H16, H17
H16	3.53–3.57, m	H15, H18
H17	1.82–1.92, m	H15, H18, H19
H18	1.82–1.92, m	H16, H17, H20, H21
H19	3.09–3.14, m	H17, H20
H20	3.53–3.57, m	H18, H19
H21	3.06, s	H18

S4. Copy of mass spectrum.

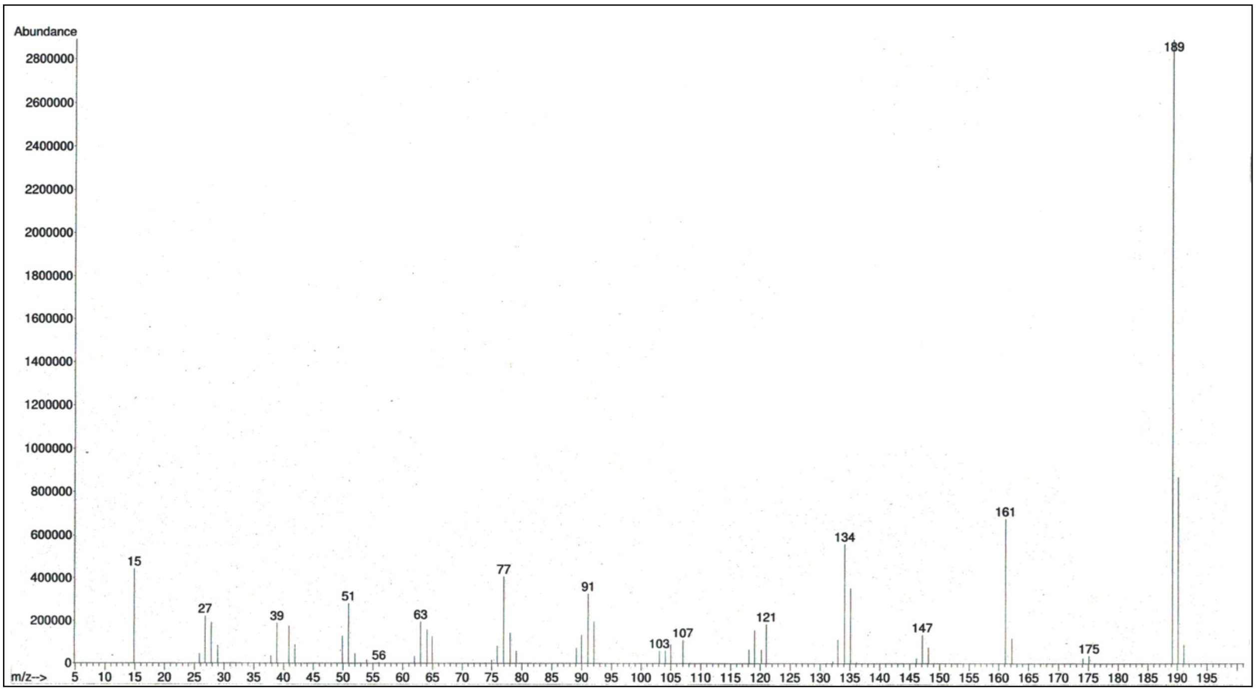


Figure S11 Mass spectrum of 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane.

S5. Elemental analysis

The mass fractions of N, H and C were determined using a Vario Micro Cube automatic elemental analyzer. The sample mass was in the range of 0.8–1 mg. The burning temperature was about 1320 K. The flash temperature in a tin capsule with the sample reached 2070 K. Helium was used as a transport gas with a flow rate of 120 ml min^{-1}. The degradation products were separated in a gas chromatography column. The N, H and C content was calculated automatically by the instrument software. The calibration coefficients were determined in experiments with standard substances; the results of the bulk experiment and the sample masses were taken into account in the software. Found (wt%): C, 69.54 ± 0.2; H, 7.30 ± 0.3; N, 14.89 ± 0.3. Calc. for $C_{11}H_{14}N_2O$ (wt%): C, 69.45; H, 7.42; N, 14.73. The MPDABH sample has a purity of 100.00 ± 0.04 wt%, estimated gravimetrically from the gaseous combustion product carbon dioxide.[S4]

S6. Differential scanning calorimetry (DSC)

Thermal analysis and determination of melting characteristics of MPDABH were carried out on a NETZSCH DSC 204 F1 Phoenix® differential scanning calorimeter (Selb, Germany) and a NETZSCH TG 209 F1 Iris® thermobalances (Selb, Germany). The instruments were pre-calibrated against temperatures and enthalpies of phase transitions of pure (99.99+%) standard substances in accordance with ASTM Practices E967, E968, E1582 and E2253. Experimental data were processed in NETZSCH Proteus® software in accordance with ASTM E794, E2550 and ISO 11357-1. RMSD for determining the temperature, heat effect and mass were 0.2 K, 5% and 0.2%, respectively.

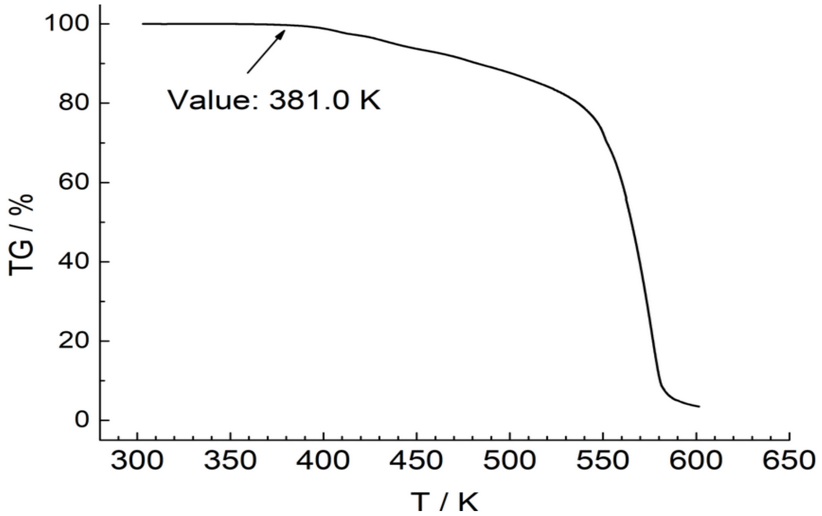


Figure S12 Thermogravimetric curve of MPDABH.

S7. Combustion calorimetry

The calorimeter, auxiliary equipment and procedure were described previously.[S5] The temperature increase of ~1 K (1 K corresponds to 0.196269 Ω) was measured using a copper resistance thermometer ($R_{298} \sim 50\ \Omega$) and a bridge circuit[S5] with a sensitivity of ~5×10^{-5} K. The calorimeter was calibrated by burning benzoic acid (grade K-1, D. I. Mendeleev Research Institute of Metrology), which has a specific combustion energy under certified conditions of −26434.4 J g^{-1} (combined expanded uncertainty $U_c = 0.6$ J Ω^{-1} at a confidence level of 0.95). The correction for small deviations from these conditions was calculated using the Jessup formula.[S5]

The experiments were organized in a series of eight and seven experiments with combined expanded uncertainties of $U_c[\varepsilon\text{I (calor.)}] = 5.8$ J Ω^{-1} and $U_c[\varepsilon\text{II (calor.)}] = 5.2$ J Ω^{-1}, respectively, at a confidence level of 0.95.

The combustion conditions of MPDABH were preliminarily selected using a Parr 6200 calorimeter. The sample (~0.12 g) was pressed into pellets using a Carver hydraulic press, sealed in Terylene film bags and burned together with the pellet of benzoic acid (~0.32 g). Weighing was performed on a Mettler M58 A balance with a standard uncertainty u(m) = 0.002 mg. Distilled water (0.002 dm^3) was added to the bomb and charged with purified oxygen (99.999 vol%) to a pressure of 3.04 MPa. The sample was ignited using a platinum wire with a diameter of 0.1 mm, heated by a capacitor discharge. The ignition energy was constant in all experiments. The initial temperature in the experiments was 298.15 K with a standard uncertainty (u) = 0.03 K.

After combustion of MPDABH, carbon dioxide in the gaseous combustion products was quantitatively determined by the gravimetric method.[S5] The CO_2 content in the combustion products was 99.96–100.01 wt%. Qualitative reactions for gaseous CO and NO + NO_2 with indicator tubes according to TU 12.43.20-76 with a sensitivity of 6×10^{-6} and 1.6×10^{-6} g, respectively, gave negative results within their sensitivity limits. The content of aqueous HNO_3 formed in the final solution was determined by titration of wash water with an aqueous solution of ~0.1 N NaOH.

Table S3 Calorimetric determination of the combustion energy of MPDABH, $C_{11}H_{14}N_2O$(cr).[a]

Experiment[b]	1	2	3	4	5
m/g	0.117751	0.121146	0.120922	0.128595	0.130136
$m_{(\text{b.a.})}$/g	0.356227	0.333755	0.326306	0.318423	0.316189
$m_{(\text{f})}$/g	0.023304	0.018104	0.021505	0.025824	0.025937
$\Delta R_{\text{corr}}/\Omega$	0.238743	0.021505	0.226342	0.228877	0.228827
$\varepsilon_{\text{f(Cont.)}}$/J Ω^{-1}	88.5	88.2	88.2	88.2	88.3
$-\Delta U_{(\text{IBP})}$/J	13924.7	13328.2	13188.3	13346.8	13343.9
$\Delta U_{(\text{b.a.})}$/J	9409.5	8815.9	8619.2	8411.0	8352.0
$\Delta U_{(\text{f})}$/J	534.3	415.1	493.1	592.1	594.7
$\Delta U_{(\text{HNO3})}$/J	14.3	13.8	10.6	13.7	15.0
$\Delta U_{\sum}$/J	10.5	9.9	9.8	9.8	9.8
$(-\Delta_c u°)_i$/J g^{-1}	33597.2	33624.7	33627.5	33595.4	33598.7
$(-\Delta_c u°)$/J g^{-1}			33609 ± 20		
$[m(CO_{2\ \text{exp}})/m(CO_{2\ \text{theor}})]_i$ (%)	99.98	99.96	100.01	-	99.96
$[m(CO_{2\ \text{exp}})/m(CO_{2\ \text{theor}})]$ (%)			100.00 ± 0.04		

[a] Molar mass is 190.246 ± 0.001 g mol^{-1},[S6] ρ = 1.240 g cm^{-3},[S3] $p°$ = 101.3 ± 0.5 kPa at T = 298.15 ± 0.01 K; the standard uncertainties are given for these values. [b] For the parameters listed below, the standard uncertainty (u) or combined expanded uncertainty (U_c) at a confidence level of 0.95 are as follows: m is the mass of the substance burned in the experiment, u = 0.002 mg; $m_{(\text{b.a.})}$ is the mass of benzoic acid, u = 0.002 mg; $m_{(\text{f})}$ is the mass of the polyester film, u = 0.002 mg; ΔR_{corr} is the increase in thermometer resistance corrected for heat exchange, $u = 1 \times 10^{-5}\ \Omega$; $\varepsilon_{\text{f(Cont.)}}$ is the energy equivalent of the bomb contents in the final state, U_c = 0.2 J Ω^{-1}; $-\Delta U_{(\text{IBP})}$ is the change in internal energy for the isothermal bomb process, $\varepsilon_{\text{I(Calor.)}}$ = 58226.2 J Ω^{-1}, U_c = 5.8 J (exp. 1 and 2), and $\varepsilon_{\text{II(Calor.)}}$ = 58226.2 J Ω^{-1}, U_c = 5.2 J (exp. 3–5); $U_{(\text{b.a.})}$ is the correction for the energy of combustion of benzoic acid, U_c = 0.2 J (calculated using $\Delta_c u°_{(\text{b.a.})} = -26414.4 \pm 0.6$ J g^{-1} (this value was obtained from the certificate value by adding a correction for conversion to the standard state);[S7] $U_{(\text{f})}$ is the correction for the energy of combustion of the sample, $\Delta_c u° = -22927.9$ J g^{-1}, U_c = 6.3 J g^{-1}; $U_{(\text{HNO3})}$ is the correction for the heat of formation of $HNO_3(aq)$ from N_2(g), O_2(g) and H_2O(l), U_c = 0.1 J (based on the molar energy of formation $\Delta_f U°(HNO_3, aq) = -59.2$ kJ mol^{-1};[S10] $U_{\sum}$ is the correction to the standard state,[S7] u = 0.1 J; $(-\Delta_c u°)_i$ is the standard specific energy of combustion of the sample; $-\Delta_c u°$ is the average value of the standard specific energy of combustion, U_c = 20 J g^{-1}; $[m(CO_{2\ \text{exp}})/m(CO_{2\ \text{theor}})]_i$ is the ratio of the mass of CO_2 determined experimentally to the mass calculated theoretically; $m(CO_{2\ \text{exp}})/m(CO_{2\ \text{theor}})$ is the average ratio of the mass of CO_2 determined experimentally to the mass calculated theoretically, $U_c = 4 \times 10^{-2}$ (wt%).

The change in internal energy for the isothermal bomb process [$-\Delta U_{(\mathrm{IBP})}$] was calculated according to

$$-\Delta U(_{\mathrm{IBP}}) = [\varepsilon_{(\mathrm{Calor.})} + \varepsilon_{f(\mathrm{Cont.})}] \times \Delta R_{\mathrm{corr}}. \tag{S1}$$

The standard specific energy of combustion of MPDABH, $-(\Delta_c u°)_i$, was calculated based on the sample mass using the following formula:

$$-(\Delta_c u^{\circ})_i = [(-\Delta U_{(\mathrm{IBP})}) - \Delta U_{(\mathrm{b.a.})} - \Delta U_{(\mathrm{f})} - \Delta U_{(\mathrm{HNO3})} - \Delta U_{\Sigma}] \times m^{-1}. \tag{S2}$$

Correction of the obtained results to the standard state was applied using the known procedure.[S7]

The standard molar energy, $\Delta_{\mathrm{c}} U_{\mathrm{m}}^{\circ}(\mathrm{cr})$, and the enthalpy of combustion, $\Delta_{\mathrm{c}} H_{\mathrm{m}}^{\circ}(\mathrm{cr})$, of MPDABH in the crystalline state were calculated from the reaction

$$C_{11}H_{14}N_2O(cr) + 14O_2(g) = 11CO_2(g) + 7H_2O(l) + N_2(g) \tag{S3}$$

and the standard molar enthalpies of formation of $CO_2(g)$ (-393.51 ± 0.13 kJ mol^{-1}) and $H_2O(l)$ (-285.83 ± 0.04 kJ mol^{-1})[S11] (Table 1, see main article).

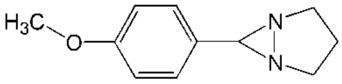
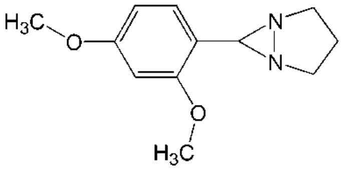
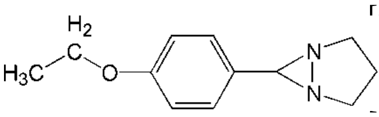
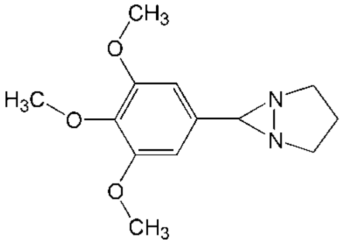
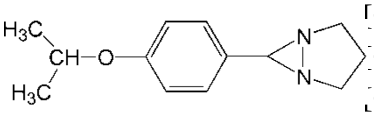
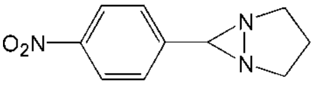
S8. Theoretical calculations

Table S4 Standard molar gas-phase enthalpy of formation of PDABH derivatives at 298.15 K calculated at the DLPNO-CCSD(T_1)/CBS//B3LYP-D3(BJ)/def2-TZVPP level using isodesmic reactions.

Entr	Reaction[a]	$\Delta_r H^\circ_m$/k	$\Delta_f H^\circ_m$/kJ
$C_{12}H_{16}N_2O_2$, 6-(2,4-dimethoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane (**I**)			
1	**I** + 6CH_4 = 3C_2H_6 + 2C_2H_4 + $C_8H_{10}O_2$[b] + NH_2NH_2	136.2	37.6
2	**I** + 6CH_4 = 2C_2H_6 + 2EtOMe + C_2H_4 + C_6H_6 + NH=NH	139.1	40.2
3	**I** + 4CH_4 + 2C_2H_6 = C_6H_6 + 2Et_2O + 2C_2H_4 + 2$MeNH_2$	68.4	41.0
4	**I** + 4CH_4 + C_2H_6 = 2Me_2O + C_8H_{10}[c] +Me_2NNH_2 + 2C_2H_4	184.4	36.2
5	**I** + 2CH_4 + C_2H_6 = C_6H_{10}[d] + PhOMe+ Me_2O + $MeNHNH_2$	72.8	39.4
6	Weighted average		39.2 ± 5.4[e]
$C_{12}H_{16}N_2O$, 6-(4-ethoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane (**II**)			
7	**II** + 6CH_4 = 3C_2H_6 + Et_2O + C_2H_4 + C_6H_6 + NH=NH	121.3	158.2
8	**II** + 6CH_4 = 3C_2H_6 + 2C_2H_4 + PhOEt + NH_2NH_2	136.9	158.9
9	**II** + 6CH_4 = C_2H_6 + MeOEt + 2C_2H_4 + PhMe + 2$MeNH_2$	101.3	156.6
10	**II** + 6CH_4 = 3C_2H_6 + 2C_2H_4 + PhOMe + $MeNHNH_2$	168.0	156.1
11	**II** + 2CH_4 = C_6H_{10}[d] + PhOH + Me_2NNH_2	20.8	158.5
12	Weighted average		157.6 ± 3.4[e]
$C_{13}H_{18}N_2O_3$, 6-(3,4,5-trimethoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane (**III**)			
13	**III** + 7CH_4 = 3C_2H_6 + 2C_2H_4 + $C_8H_{10}O_2$[b] +Me_2O + NH_2NH_2	150.2	−85.9
14	**III** + 7CH_4 = 2C_2H_6 + 2EtOMe + Me_2O + C_2H_4 + C_6H_6 + NH=NH	153.1	−83.3
15	**III** + 5CH_4 + 2C_2H_6 = C_6H_6 + 2Et_2O + Me_2O + 2C_2H_4 + 2$MeNH_2$	82.4	−82.5
16	**III** + 5CH_4 + C_2H_6 = 3Me_2O + C_8H_{10}[c] + Me_2NNH_2 + 2C_2H_4	198.4	−87.2
17	**III** + 3CH_4 + C_2H_6 = C_6H_{10}[d] + PhOMe + 2Me_2O + $MeNHNH_2$	86.8	−84.1
18	Weighted average		−84.3 ± 5.4[e]
$C_{13}H_{18}N_2O$, 6-(4-isopropoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane (**IV**)			
19	**IV** + 6CH_4 = 3C_2H_6 + Et_2O + C_2H_4 + PhMe + NH=NH	123.2	123.1
20	**IV** + 7CH_4 = 4C_2H_6 + 2C_2H_4 + PhOEt + NH_2NH_2	160.2	126.1
21	**IV** + 6CH_4 = *n*-C_4H_{10} + EtOMe + 2C_2H_4 + C_6H_6 + 2$MeNH_2$	123.9	125.5
22	**IV** + 8CH_4 = 5C_2H_6 + 2C_2H_4 + PhOH + $MeNHNH_2$	157.7	125.2
23	**IV** + 2CH_4 = C_6H_{10}[d] + PhOMe + Me_2NNH_2	77.8	123.6
24	Weighted average		124.7 ± 3.6[e]
$C_{10}H_{11}N_3O_2$, 6-(4-nitrophenyl)-1,5-diazabicyclo[3.1.0]hexane (**V**)			
25	**V** + 7CH_4 = C_6H_6 + $MeNO_2$ + NH=NH + C_2H_4 + 4C_2H_6	126.8	322.9
26	**V** + 6CH_4 = $PhNO_2$ + NH_2NH_2 + 2C_2H_4 + 3C_2H_6	138.9	324.1
27	**V** + C_4H_4O[f] + 6CH_4 = $C_4H_3NO_3$[g] + C_6H_6 + 2$MeNH_2$ + 2C_2H_4 + 2C_2H_6	106.6	324.0
28	**V** + CH_4 + C_2H_6 = C_6H_{10}[d] + $PhNO_2$ + $MeNHNH_2$	32.4	325.2
29	**V** + 5CH_4 = C_6H_6 + $MeNO_2$ + Me_2NNH_2 + 2C_2H_4 + C_2H_6	166.0	322.8
30	Weighted average		323.7 ± 2.7[e]

[a] The $\Delta_f H^\circ_m$(298.15 K) values for reference species were taken from the Active Thermochemical Tables (ATcT)[S8] and from the original works for $MeNHNH_2$, Me_2NNH_2, furan,[S9] bicyclo[3.1.0]hexane,[S10] 1,3- and 1,4-dimethoxybenzene,[S11] PhOEt[S12] and nitrofuran.[S13] [b] 1,3-Dimethoxybenzene. [c] 1,4-Dimethylbenzene. [d] Bicyclo[3.1.0]hexane. [e] The uncertainty of calculated values were defined as $s_d \times t$, where s_d is the standard deviation from the weighted average value and t is Student's coefficient for the 95% confidence level. [f] Furan. [g] Nitrofuran.

Table S5 Gas- and solid-phase enthalpies of formation of PDABH derivatives at 298.15 K calculated using group additivity method.

Molecule	Group[a]	No. of groups	Group values	
			$\Delta_f H^\circ_m$(cr)/kJ·mol^{-}	$\Delta_f H^\circ_m$(g)/kJ·mol
	$\Delta_f H^\circ_m$(PDABH)	1	246.4	343.4
	$[C_B\text{-}(C_B)_2(H)]$	1	-6.53	-13.81
	$[C_B\text{-}(C_B)_2(O)]$	1	1.00	-4.75
	$[O\text{-}(C_B)(C)]$	1	-122.87	-92.55
	$[C\text{-}O)(H)_3]$	1	-46.74	-42.26
		∑ =	71.3	190.0
	$\Delta_f H^\circ_m$(PDABH)	1	246.4	343.4
	$[C_B\text{-}(C_B)_2(H)]$	2	-6.53	-13.81
	$[C_B\text{-}(C_B)_2(O)]$	2	1.00	-4.75
	$[O\text{-}(C_B)(C)]$	2	-122.87	-92.55
	$[C\text{-}(O)(H)_3]$	2	-46.74	-42.26
	MeO-COOH	1	5.00	5.00
		∑ =	-98.9	41.7
	$\Delta_f H^\circ_m$(PDABH)	1	246.4	343.4
	$[C_B\text{-}(C_B)_2(H)]$	1	-6.53	-13.81
	$[C_B\text{-}(C_B)_2(O)]$	1	1.00	-4.75
	$[O\text{-}(C_B)(C)]$	1	-122.87	-92.55
	$[C\text{-}(H)_2(O)(C)]$	1	-33.00	-32.9
	$[C\text{-}(O)(H)_3]$	1	-46.74	-42.26
		∑ =	38.3	157.1
	$\Delta_f H^\circ_m$(PDABH)	1	246.4	343.4
	$[C_B\text{-}(C_B)_2(H)]$	3	-6.53	-13.81
	$[C_B\text{-}(C_B)_2(O)]$	3	1.00	-4.75
	$[O\text{-}(C_B)(C)]$	3	-122.87	-92.55
	$[C\text{-}(O)(H)_3]$	3	-46.74	-42.26
	MeO-COOH	2	23.00	15.00
		∑ =	-233.0	-86.7
	$\Delta_f H^\circ_m$(PDABH)	1	246.4	343.4
	$[C_B\text{-}(C_B)_2(H)]$	1	-6.53	-13.81
	$[C_B\text{-}(C_B)_2(O)]$	1	1.00	-4.75
	$[O\text{-}(C_B)(C)]$	1	-122.87	-92.55
	$[C\text{-}(H)(O)(C)_2]$	1	-20.08	-19.46
	$[C\text{-}(C)(H)_3]$	2	-46.74	-42.26
		∑ =	4.4	128.3
	$\Delta_f H^\circ_m$(PDABH)	1	246.4	343.4
	$[C_B\text{-}(C_B)_2(H)]$	1	-6.53	-13.81
	$[C_B\text{-}(NO_2)(C_B)_2]$	1	-32.50	-1.45
		∑ =	207.4	328.1

[a] Group values determined by Domalski and Hearing.[S14] The positive values of $[C_B\text{-}(C_B)_2(H)]$ groups are given with a negative sign, since they were subtracted from the values of $\Delta_f H^\circ_m$(PDABH) determined[S5] in the gas and solid state and were replaced by the corresponding contributions of the substitutes.

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