Electronic supplementary information

Enthalpy of formation of 6-phenyl-1,5-diazabicyclo[3.1.0]hexane by combustion calorimetry. Theoretical approach for efficient prediction of thermochemistry of diaziridines

Vera A. Lukyanova,[a] Vladimir V. Kuznetsov,[b] Natalia M. Konstantinova,[a] Andrey S. Dmitrenok,[b] Maria P. Kosaya,[a] Olga V. Dorofeeva* [a] and Anna I. Druzhinina[a]

[a] *Department of Chemistry, M.V. Lomonosov Moscow State University, 119991 Moscow, Russia. E-mail: dorofeeva@phys.chem.msu.ru.*

[b] *N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russia.*

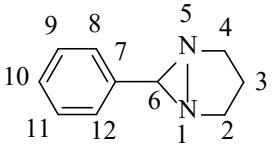
Contents **page**

S1 Spectral characteristics

General remarks. Spectra of NMR were recorded on Bruker Avance 600 spectrometers at room temperature; the chemical shifts δ were measured in ppm with respect to solvent ($CDCl_3$: ^1H: δ = 7.26 ppm, ^{13}C: δ = 77.0 ppm). Splitting patterns are designated as s, singlet; m, multiplet. Coupling constants (*J*) are given in Hz. The structures of synthesized compounds were elucidated with the aid of 1D NMR (^1H, ^{13}C) and 2D NMR (HSQC and HMBC ^1H-^{13}C, NOESY ^1H-^1H) spectroscopies. The 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 a positive (+MS) ion mode (interface capillary voltage: 4500 V) with scan range m/z: 50-3000. External calibration of the mass spectrometer was performed with Electrospray Calibrant Solution (Fluka). A direct syringe injection was used for all analyzed solutions in MeCN (flow rate: 3 μL min^{-1}). Mass spectra were also measured using a Finnigan MAT INCOS-50 instrument. Melting point (mp) was determined using Electrothermal 9100 and SMP-20 capillary melting point apparatus; its value is 92.70 °C (365.85 K); literature data are 88-89 °C [1], 93-94 °C [2,3].

References

1. Yu.B. Koptelov, M.Kh.Kim, , A.P. Molchanov, R.R. Kostikov, Russ. J. Org. Chem. 35 (1999) 110–118.
2. A.P. Molchanov, D.I. Sipkin, Yu.B. Koptelov, R.R. Kostikov, Russ. J. Org. Chem. 37 (2001), 841–851.
3. V.V. Kuznetsov, S.A. Kutepov, N.N. Makhova, K.A. Lyssenko, D.E. Dmitriev, Russ. Chem. Bull. 52 (2003) 665–673.

NMR, IR and mass spectra of PDABH. ^1H NMR ($CDCl_3$, 600.13 MHz): *δ* = 1.84−1.95 (m, 2 H, 

$H_2C(3)$), 3.11 (s, 1 H, HC(6)), 3.12−3.18 (m, 2 H, $H_aC(2)$, $H_aC(4)$), 3.56−3.61 (m, 2 H, $H_bC(2)$, $H_bC(4)$), 7.28−7.36 (m, 5 H, HC(8), HC(9), HC(10), HC(11), HC(12)). **^{13}C NMR** ($CDCl_3$, 150.90 MHz): δ = 21.6 C(3), 52.2 C(2), C(4), 56.6 C(6), 127.2 C(8), C(12), 128.2 C(9), C(11), 128.4 C(10), 137.0 C(7). **IR** (KBr): ν = 3449, 3063, 2980, 2943, 2874, 2329, 2014, 1991, 1940, 1917, 1868, 1843, 1794, 1780, 1696, 1624, 1598, 1536, 1492, 1458, 1391, 1331, 1313, 1287, 1175, 1074, 1018, 970, 954, 910, 871, 845, 762, 706, 660, 601, 513 cm^{-1}. **HRMS** (ESI-TOF): m/z calcd. for $C_{10}H_{12}N_2^+$: 161.1073 $[M+H]^+$; found: 161.1078. **Mass-spectra** (EI, 70 eV), m/z: 160 (13) $[M]^+$, 132 (3) $[M - 2\ CH_2]^+$, 131 (29) $[M - 2\ CH_2 - H]^+$, 118 (3) $[M - 3\ CH_2]^+$, 117 (2) $[M - 3\ CH_2 - H]^+$, 104 (22) $[M - 3\ CH_2 - N]^+$, 103 (8) $[M - 3\ CH_2 - N - H]^+$, 90 (7) $[M - 3\ CH_2 - 2\ N]^+$, 89 (13) $[M - 3\ CH_2 - 2\ N - H]^+$, 78 (4) $[C_6H_6]^+$, 77 (21) $[Ph\text{-}]^+$.

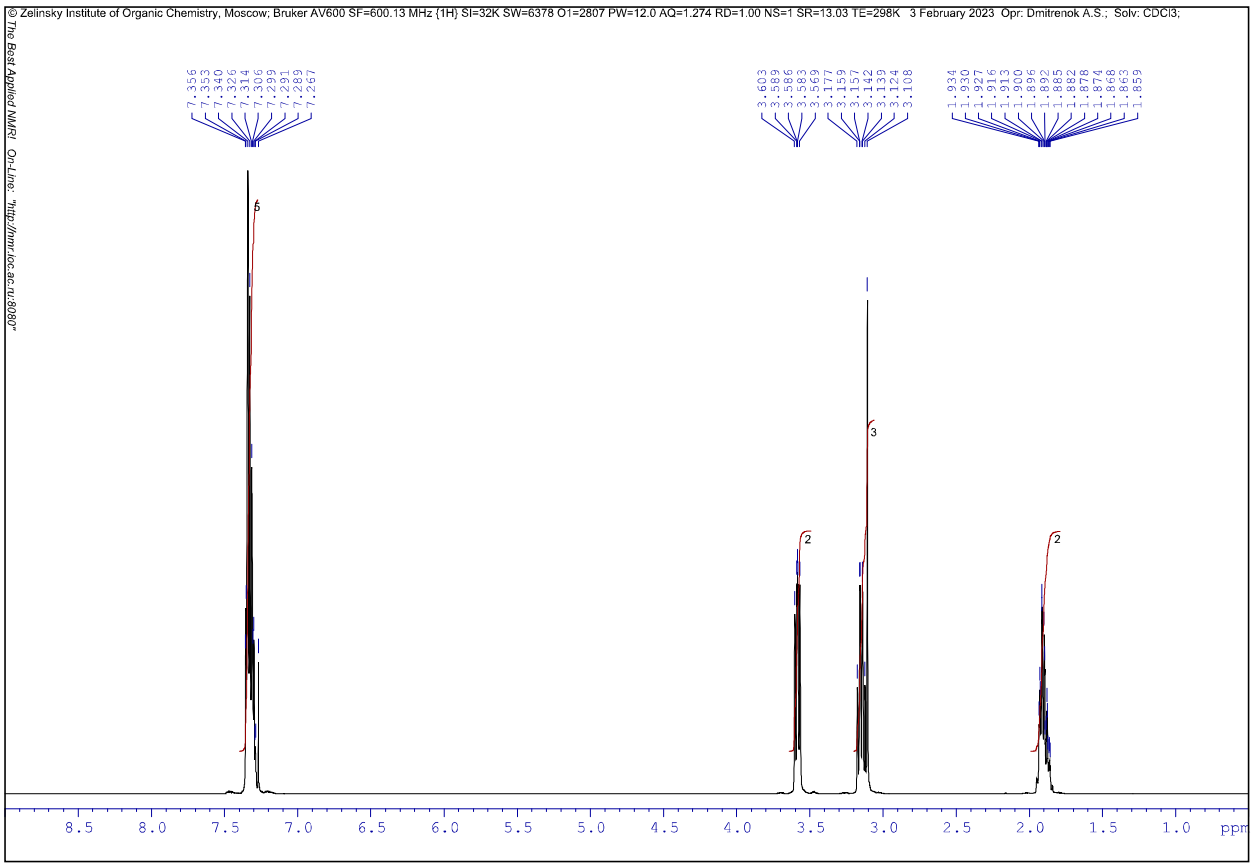


Fig. S1 ^{1}H NMR spectrum of PDABH ($CDCl_3$).

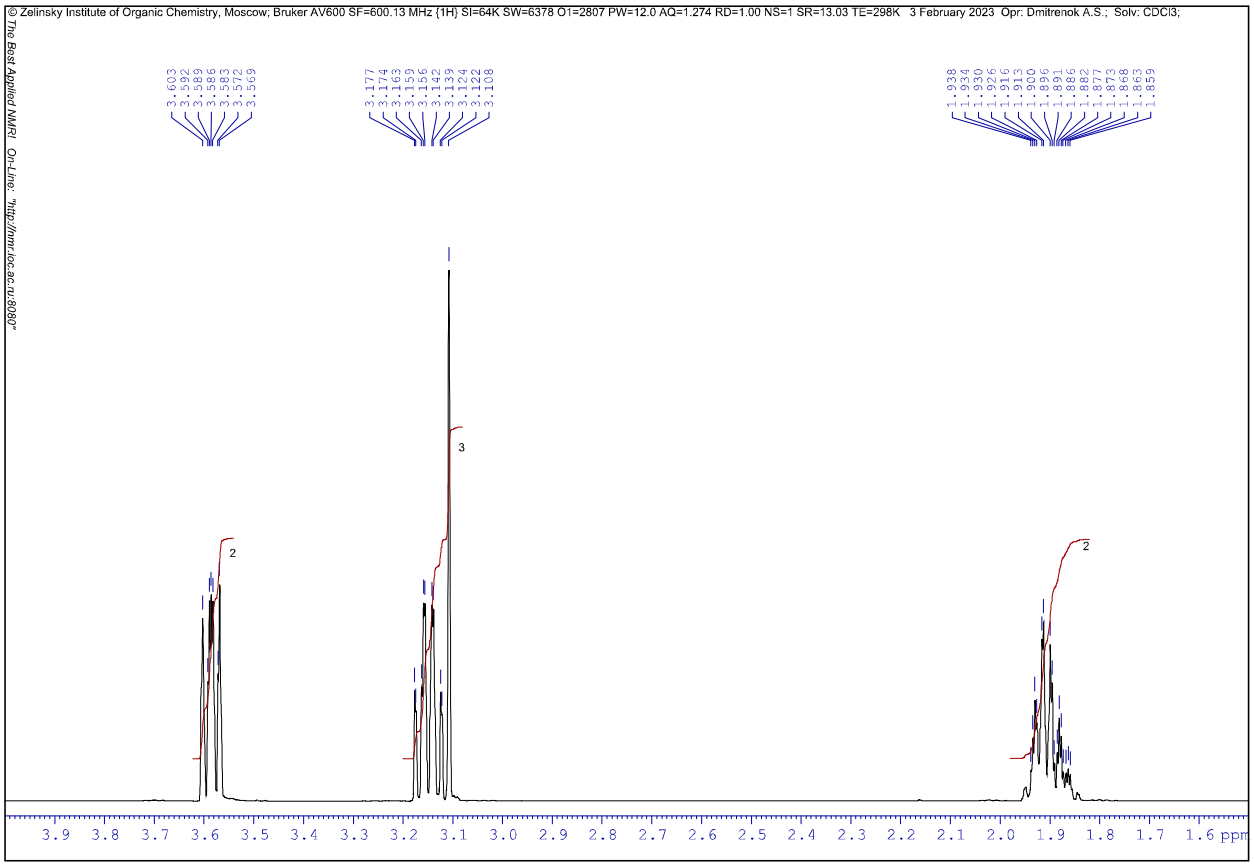


Fig. S2 Fragment 1 of the ^{1}H NMR spectrum of PDABH ($CDCl_3$).

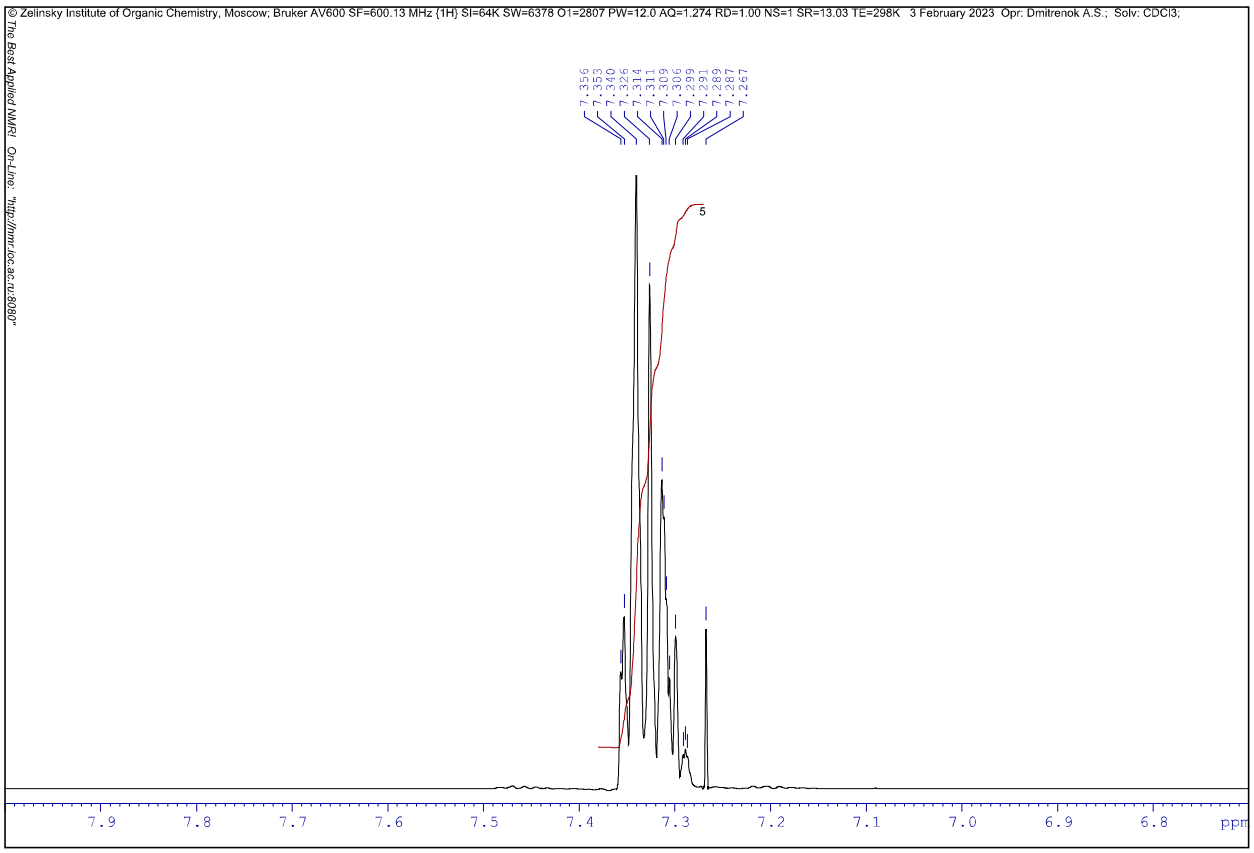


Fig. S3 Fragment 2 of the ^{1}H NMR spectrum of PDABH ($CDCl_3$).

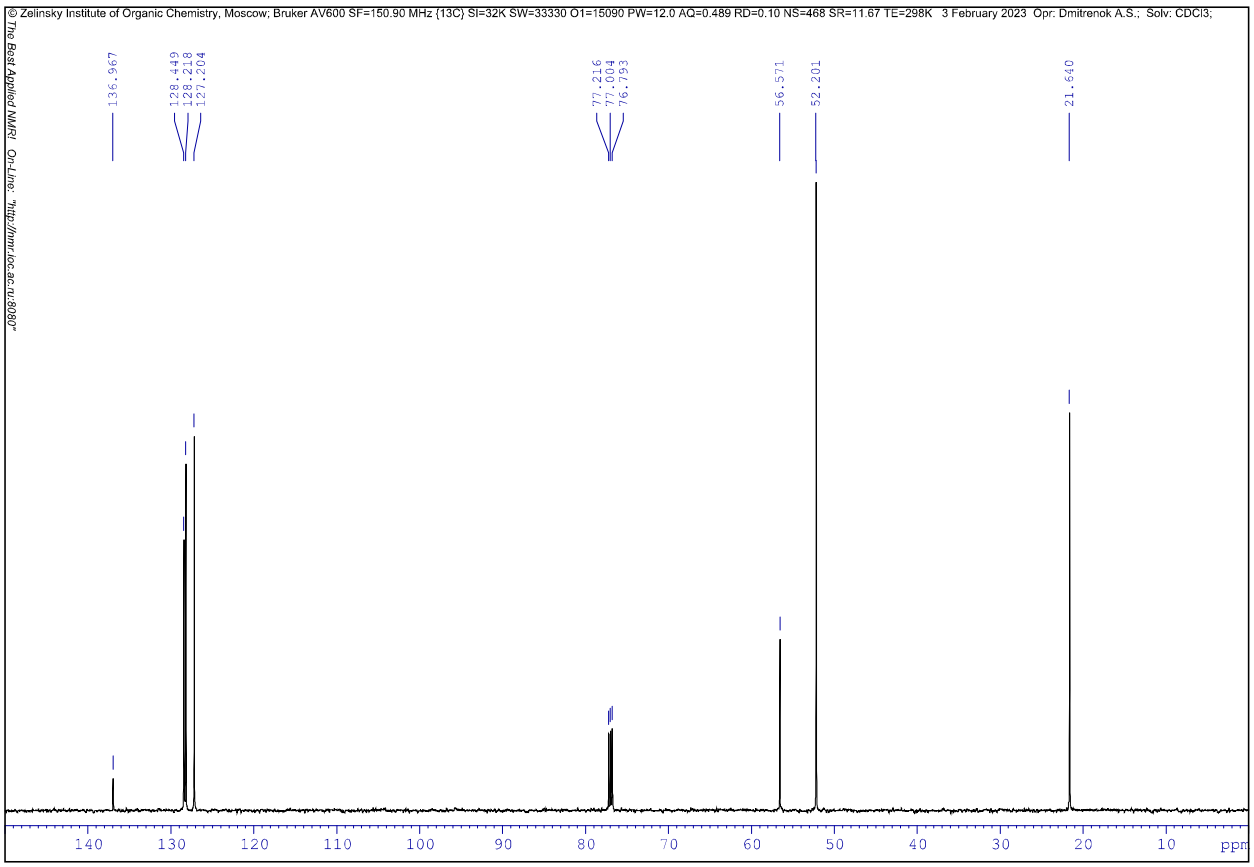


Fig. S4 ^{13}C NMR spectrum of PDABH ($CDCl_3$).

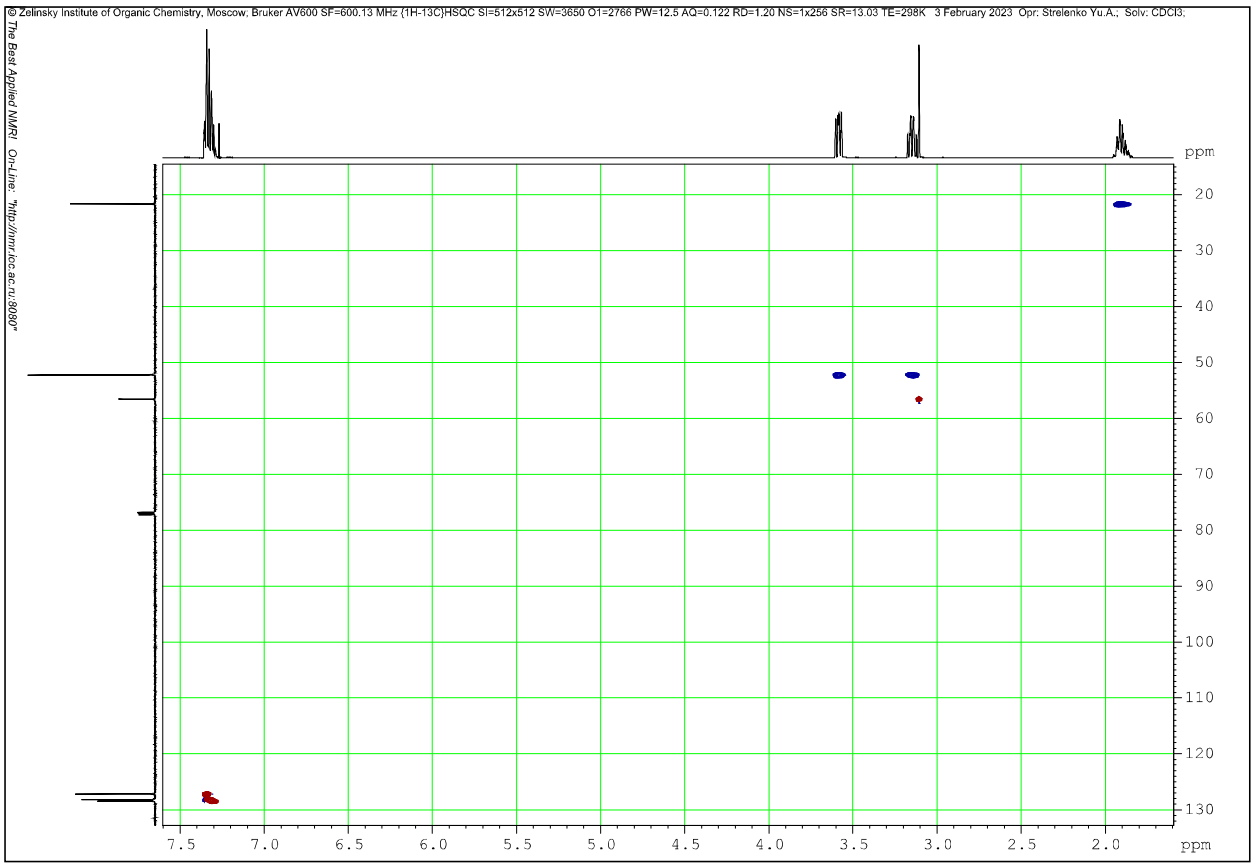


Fig. S5 {^{1}H-^{13}C}HSQC spectrum of PDABH ($CDCl_3$).

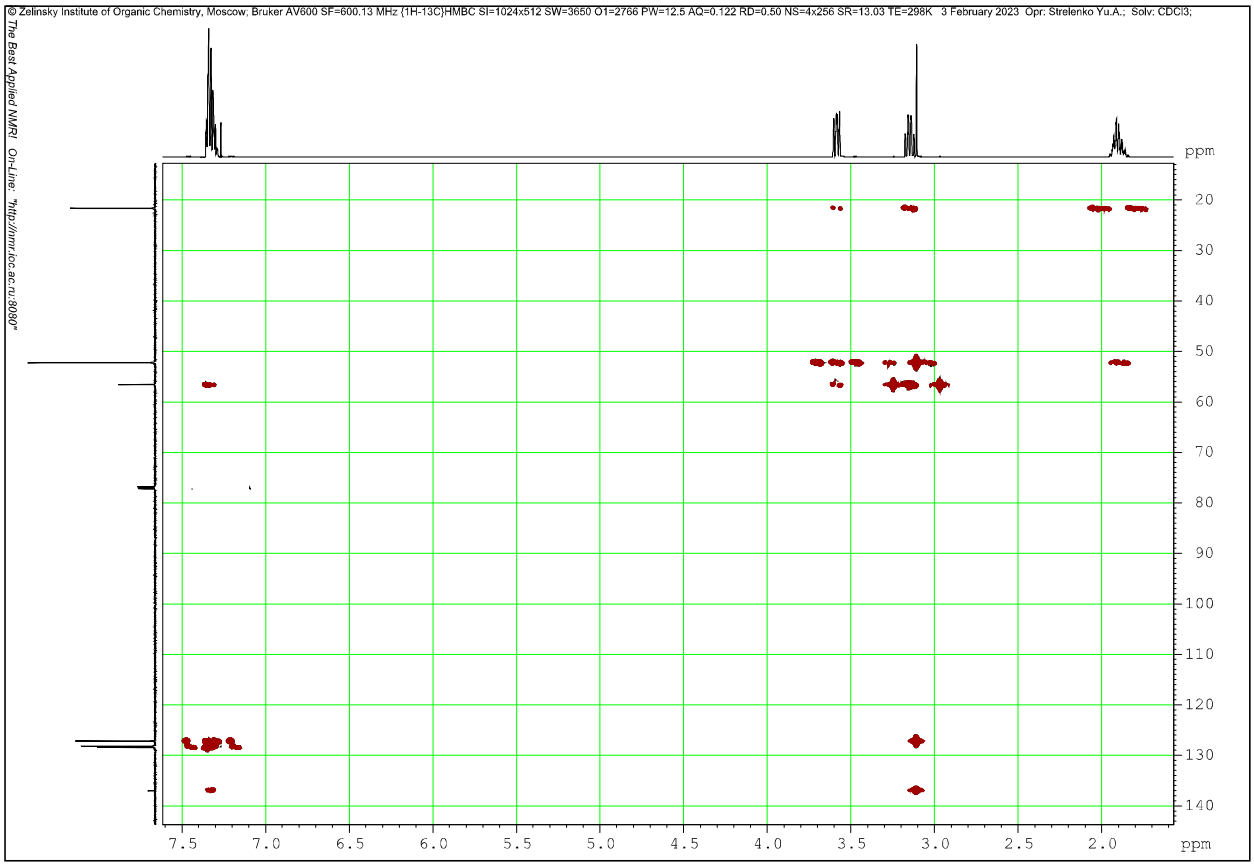


Fig. S6 {^{1}H-^{13}C}HMBC spectrum of PDABH ($CDCl_3$).

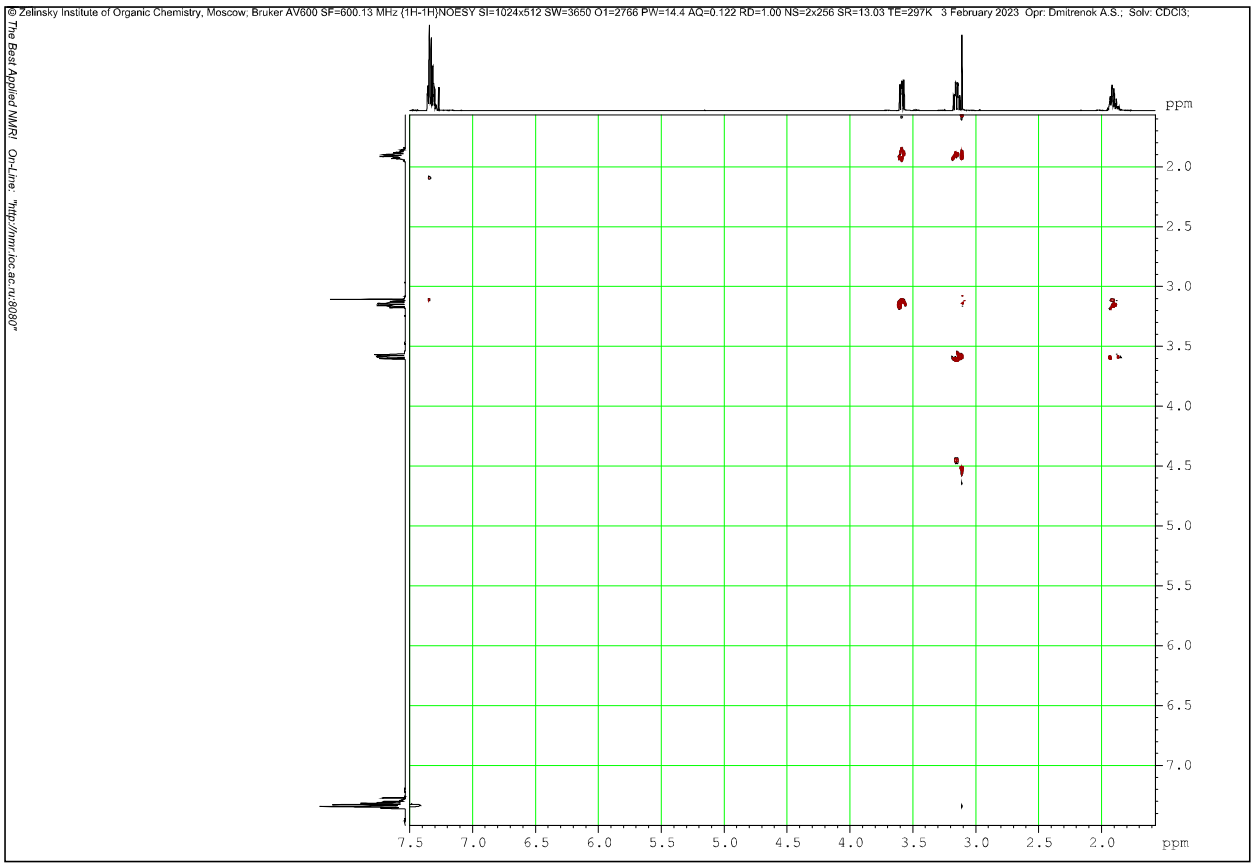


Fig. S7 $\{^1H–^1H\}$gNOESYspectrum of PDABH ($CDCl_3$).

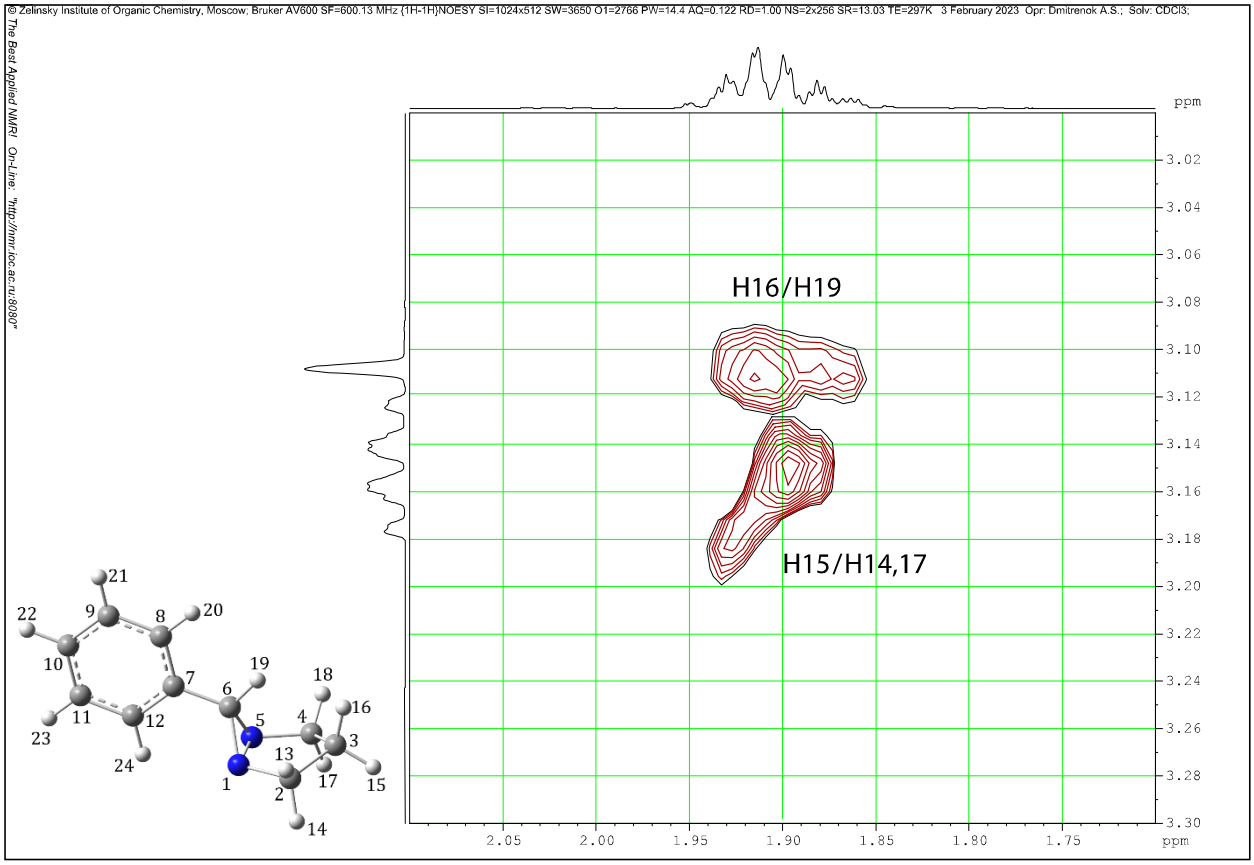


Fig. S8 Fragment of $\{^1H–^1H\}$gNOESY spectrum of PDABH ($CDCl_3$). Proton H16 has cross-peaks with proton H19. Proton H15 has cross-peaks with protons H14 and H17.

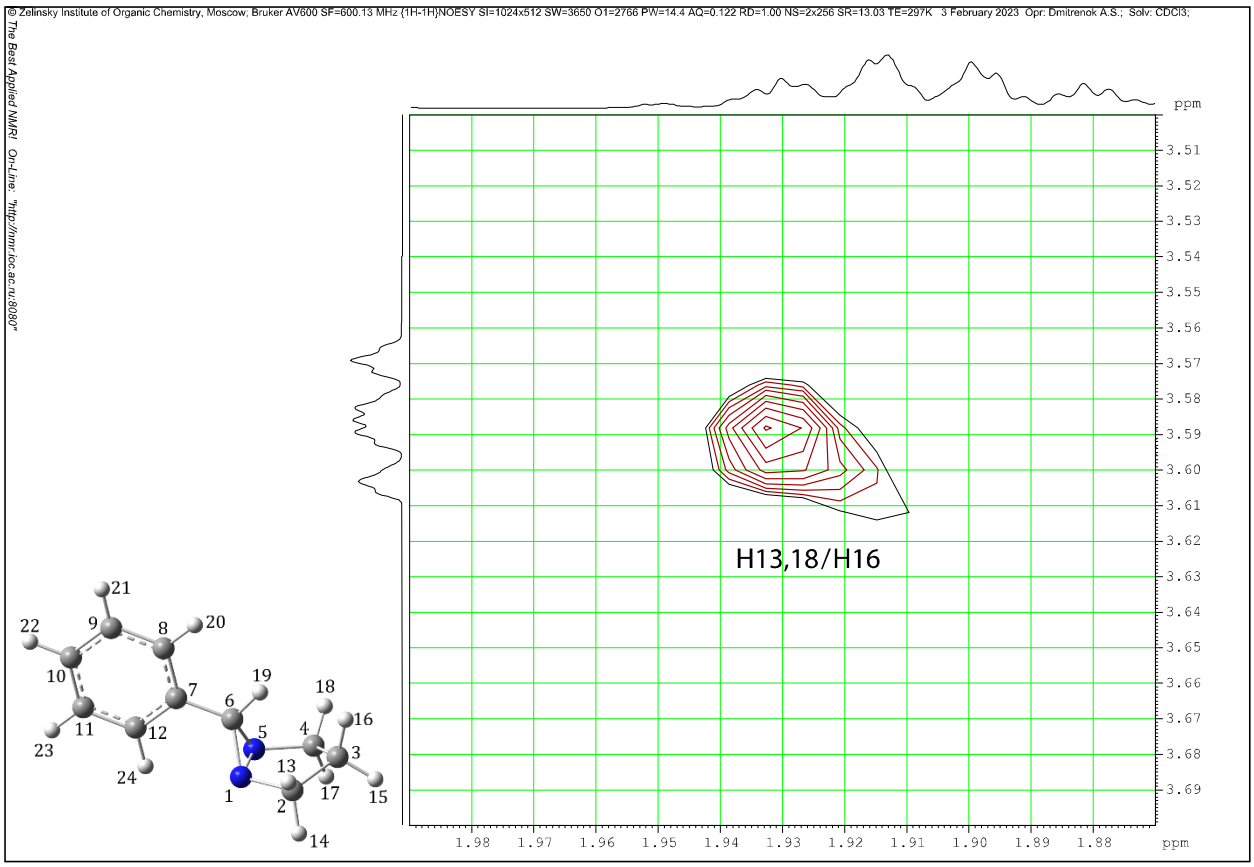


Fig. S9 Fragment of the {^{1}H–^{1}H}gNOESY spectrum of PDABH ($CDCl_3$). Proton H16 has cross-peaks with protons H13 and H18.

The data of the 2D NMR spectra

Table S1 The {^{1}H-^{13}C}HSQC, and {^{1}H-^{13}C}HMBC data for PDABH (Fig. S5, S6)

Atom numbers	^{13}C NMR chemical shift, ppm	{^{1}H-^{13}C}HSQC interactions	{^{1}H-^{13}C}HMBC interactions
C2	52.2	H13 H14	H15, H16, H17, H18, H19
C3	21.6	H15 H16	H13, H14, H17, H18
C4	52.2	H17, H18	H13, H14, H15, H16, H19
C6	56.6	H19	H13, H14, H17, H18, H20, H24
C7	137.0	-	H19, H20, H24
C8	127.2	H20	H19, H21, H22, H24
C9	128.2	H21	H20, H22, H23
C10	128.4	H22	H20, H21, H23, H24
C11	128.2	H23	H21, H22, H24
C12	127.2	H24	H19, H22, H23

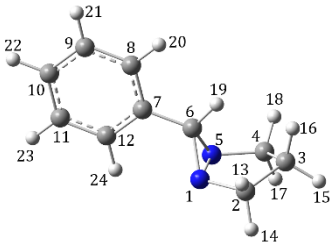
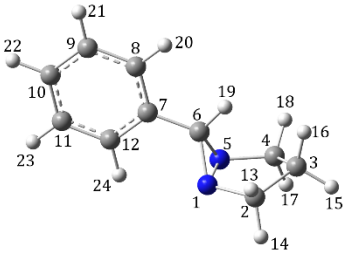


Table S2 Partial data {^{1}H- ^{1}H}gNOESY for PDABH (Fig. S7, S8, S9)

Atom numbers	^{1}H NMR chemical shift, ppm	Coupling constant, (*J* Hz)	{^{1}H-^{1}H}gNOESY Interactions
H13	3.56−3.61, m	11.8 ($^2J_{H13-H14}$)	H14, H16, H19
H14	3.12−3.18, m	11.8 ($^2J_{H14-H13}$)	H13, H15
H15	1.84−1.95, m	-	H14, H16, H17
H16	1.84−1.95, m	-	H13, H15, H18, H19
H17	3.12−3.18, m	11.8 ($^2J_{H17-H18}$)	H15,H18
H18	3.56−3.61, m	11.8 ($^2J_{H18-H17}$)	H16, H17, H19
H19	3.11, s	-	H13, H16, H18



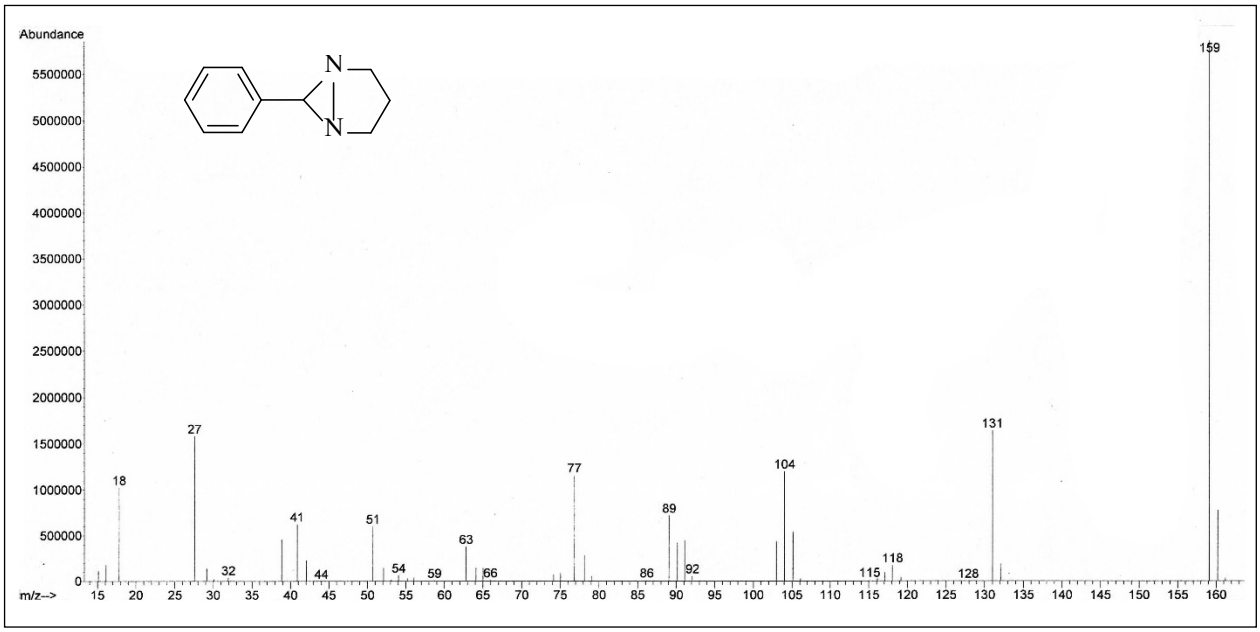


Fig. S10 Mass spectrum of PDABH.

S2 Melting characteristics of PDABH investigated by differential scanning calorimetry (DSC)

General remarks. Thermal analysis was carried out on DSC 204 F1 Phoenix ® differential scanning calorimeter (NETZSCH, Selb, Germany) and TG 209 F1 Libra ® thermobalances (NETZSCH, Selb, Germany). Samples weighing 1.00–10.00 mg were tested in aluminum (DSC) and alumina (TG) crucibles (lid with a hole) under dry nitrogen flow (20–70 mL·min^{-1}) with a heating rate of 0.5 °C·min^{-1} for DSC and 10 °C·min^{-1} for TG measurements. Instruments were previously calibrated for temperatures and enthalpies of phase transitions of pure (99.99+ %) standard substances in compliance with ASTM Practices E967, E968, E1582, and E2253: cyclohexane, adamantane, Hg,

H_2O, benzoic acid, In, Sn, Bi, Pb, Zn, CsCl – for DSC; In, Sn, Bi, Zn, Al, Ag, Au – for TG. Calcium oxalate monohydrate was used for the validation of thermobalances. RMSD for temperature, heat effect and mass determination were 0.2 °C, 5 % and 0.2 %, correspondingly. Experimental data were processed in NETZSCH Proteus ® Software according to ASTM E794, E2550, and ISO 11357-1.

Substance purity was determined by DSC according to ASTM E928 procedure. Sample was ramped at 0.5 °C·min^{-1} from 358 to 368 K. Experimental DSC signal was additionally corrected on thermal lag to obtain actual sample temperature. Thermal resistance constant was obtained from the melting curve of a high purity (99.999 %) indium standard. The melting temperature of PDABH is 365.85 ± 0.2 K (92.70 °C); the melting enthalpy is 22763.50 J·mol^{-1} (142.08 J·g^{-1}); the purity is 99.94 mol.%.

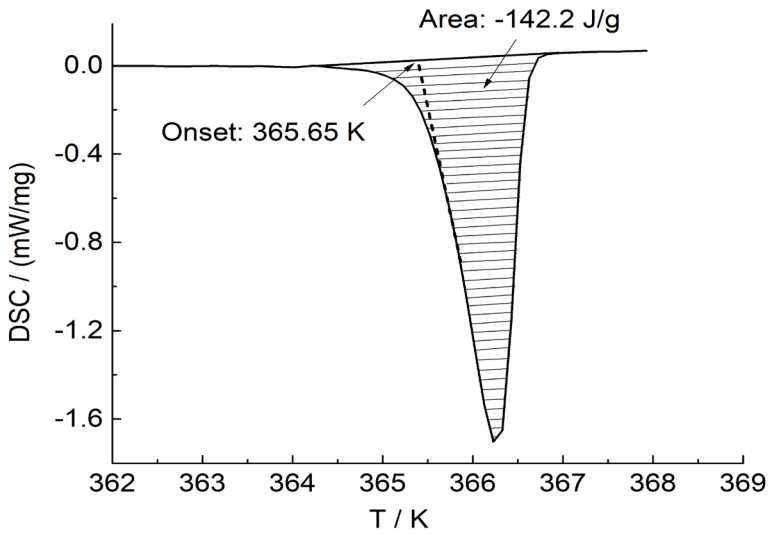


Fig. S11 DSC curve of PDABH.

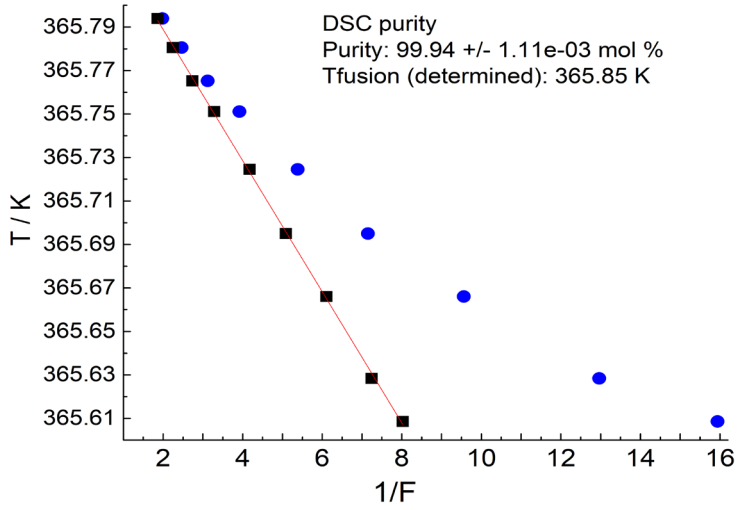
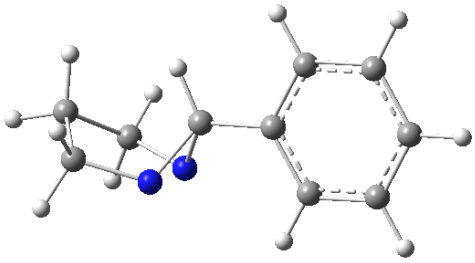


Fig. S12 The results for the fractional melting of the PDABH sample: equilibrium temperature of PDABH sample melting *T* vs 1/F, where 1/F is the reciprocal fraction of the sample melted.

S3 Theoretical calculations

Table S3 Cartesian coordinates of PDABH molecule optimized at B3LYP-D3(BJ)/def2-TZVPP level.



C_s symmetry

C	0.743594	-3.311469	0.000000
C	1.141767	-2.434628	1.197049
C	-0.050866	-0.671503	0.000000
C	1.141767	-2.434628	-1.197049
H	0.473530	-2.538932	2.051745
H	2.155241	-2.658107	1.529813
H	2.155241	-2.658107	-1.529813
H	-0.322860	-3.528787	0.000000
H	-0.865238	-1.390786	0.000000
H	0.473530	-2.538932	-2.051745
H	1.267253	-4.265181	0.000000
N	1.141767	-1.029557	-0.746316
N	1.141767	-1.029557	0.746316
C	-0.500846	0.740523	0.000000
C	-1.861592	1.035381	0.000000
C	0.424756	1.783729	0.000000
C	-2.298588	2.355194	0.000000
H	-2.583876	0.228044	0.000000
C	-0.010884	3.100409	0.000000
H	1.478759	1.547122	0.000000
C	-1.372692	3.390363	0.000000
H	-3.358145	2.573141	0.000000
H	0.711877	3.905445	0.000000
H	-1.708539	4.418654	0.000000

Table S4 Enthalpies of formation of reference species used in working reactions and DLPNO-CCSD(T1)/CBS energies, ZPEs and enthalpic corrections for the compounds studied

Molecule		$\Delta_f H_m^\circ$(298.15 K) kJ·mol^{-1}	Ref.	E_e [a] Hartree	ZPE [b] Hartree	$(H_{298}^\circ - H_0^\circ)$[b] Hartree
CH_4	CH_4	-74.52 ± 0.05	[1]	-40.459037	0.044078	0.003815
CH_4N_2	Diaziridine	235.3 ± 1.0	[2]	-149.770578	0.058280	0.004106
CH_4N_2O	$NH_2C(O)NH_2$	-234.58 ± 0.42	[1]	-225.053499	0.062842	0.005416
CH_4O	CH_3OH	-200.92 ± 0.15	[1]	-115.612461	0.050500	0.004315
CH_5N	CH_3NH_2	-21.25 ± 0.23	[1]	-95.747147	0.063085	0.004399
CH_6N_2	CH_3NHNH_2	94.6 ± 0.6	[3]	-151.010035	0.080428	0.005173
C_2H_4	CH_2=CH_2	52.38 ± 0.12	[1]	-78.476121	0.050365	0.003992
C_2H_4O	Oxirane	-52.51 ± 0.35	[1]	-153.620407	0.056602	0.004115
C_2H_5N	Aziridine	126.72 ± 0.89	[1]	-133.755511	0.069290	0.004203
C_2H_6	CH_3CH_3	-84.02 ± 0.12	[1]	-79.714152	0.073581	0.004446
C_2H_7N	CH_3NHCH_3	-17.43 ± 0.40	[1]	-134.995366	0.091038	0.005386
C_2H_7N	$CH_3CH_2NH_2$	-49.88 ± 0.46	[1]	-135.008537	0.091372	0.005386
$C_2H_8N_2$	$(CH_3)_2NNH_2$	83.8 ± 2.5	[3]	-190.263407	0.107525	0.006302
C_3H_6	Cyclopropane	53.88 ± 0.38	[1]	-117.726834	0.080232	0.004335
C_3H_6	CH_2=$CHCH_3$	20.02 ± 0.19	[1]	-117.738879	0.078566	0.005049
C_3H_6O	$CH_3C(O)CH_3$	-216.93 ± 0.27	[1]	-192.931964	0.082345	0.006386
C_3H_8	$CH_3CH_2CH_3$	-105.00 ± 0.16	[1]	-118.972715	0.101930	0.005501
$C_4H_4N_2$	Pyrazine	203.2 ± 1.5	[4]	-263.977808	0.075874	0.005141
C_4H_5N	1*H*-Pyrrole	108.2 ± 0.8	[5]	-209.893602	0.081534	0.004935
$C_4H_8N_2$	1,5-Diazabicyclo[3.1.0]-hexane	252.7 ± 2.1	[2]	-266.330395	0.120986	0.005940
C_4H_{10}	$CH_3CH_2CH_2CH_3$	-125.64 ± 0.24	[1]	-158.231393	0.130089	0.006770
$C_4H_{10}N_2$	Piperazine	26.7 ± 2.1	[6]	-263.977808	0.075874	0.005141
$C_5H_8N_2$	2,3-Diazabicyclo[2.2.1]-hept-2-ene	207.4 ± 2.7	[7]	-304.413227	0.127701	0.005996
C_5H_{10}	Cyclopentane	-76.25 ± 0.41	[1]	-196.279351	0.138737	0.006205
$C_5H_{11}N$	Piperidine	-48.8 ± 2.6	[8]	-251.575993	0.157001	0.006559
C_6H_6	Benzene	83.23 ± 0.22	[1]	-231.913115	0.099307	0.005369
C_6H_{10}	Bicyclo[3.1.0]hexane	38.6 ± 2.1	[9]	-234.301157	0.144559	0.006163
C_6H_{12}	Cyclohexane	-122.76 ± 0.29	[1]	-235.547997	0.168052	0.006705
$C_6H_{12}N_2$	1,2-Diazaspiro[2.5]octane			-344.879851	0.179190	0.008119
$C_6H_{12}N_4$	Hexamethylenetetramine	203.7 ± 0.8	[10]	-454.283612	0.195771	0.007222
C_7H_{10}	Norbornene	82.6 ± 2.1	[11]	-272.349731	0.150989	0.006221
C_7H_{12}	Norbornane	-53.6 ± 1.9	[12]	-273.588519	0.174686	0.006641
$C_8H_{14}N_2$	1,4-Dimethyl-2,3-diaza-bicyclo[2.2.2]octene-2	92.4 ± 4.4	[74]	-422.209357	0.210686	0.010247
$C_{10}H_9N$	1-Phenylpyrrole	226.4 ± 2.4	[13]	-440.610749	0.161462	0.009249
$C_{10}H_{12}N_2$	6-Phenyl-1,5-diaza-bicyclo[3.1.0]hexane			-497.059069	0.200852	0.010569
$C_{10}H_{16}$	Adamantane	-132.3 ± 2.2	[14]	-390.187355	0.240709	0.008002
$C_{12}H_{10}$	Biphenyl	179.7 ± 1.1	[15]	-462.639154	0.179473	0.009352
H_2N_2	NH=NH	199.98 ± 0.41	[1]	-110.532016	0.028000	0.003802
H_3N	NH_3	-45.56 ± 0.03	[1]	-56.505222	0.033840	0.003816
H_3NO	NH_2OH	-43.45 ± 0.42	[1]	-131.608580	0.039777	0.004171
H_4N_2	NH_2NH_2	97.57 ± 0.42	[1]	-111.758846	0.052628	0.004227

[a] DLPNO-CCSD(T_1)/CBS//B3LYP-D3(BJ)/def2-TZVPP single point energy.

[b] Calculated at B3LYP-D3(BJ)/def2-TZVPP level; ZPEs and $(H_{298}^\circ - H_0^\circ)$ corrections are calculated using vibrational frequencies scaled by 0.9883.

References

[1] B. Ruscic, D.H. Bross, Active Thermochemical Tables (ATcT), Version 1.124: Argonne National Laboratory, 2022, http://atct.anl.gov/ (accessed May 25, 2023).

[2] Calculation, this work; see Table 4.

[3] J.D. Cox, G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, New York 1970.

[4] S.P. Verevkin, V.N. Emel'yanenko, R. Notario, M.V. Roux, J.S. Chickos, J.F. Liebman, J. Phys. Chem. Lett. 3 (2012) 3454−3459.

[5] A. Das, M. Frenkel, N.A.M., Gadalla, S. Kudchadker, K.N. Marsh, A.S. Rodgers, R.C. Wilhoit, J. Phys. Chem. Ref. Data 22 (1993) 659−780.

[6] O.V. Dorofeeva, M.A. Filimonova, J. Chem. Thermodyn. 145 (2020) 106092.

[7] P.S. Engel, R.A. Melaugh, M. Månsson, J. W. Timberlake, A.W. Garner, F.D. Rossini, J. Chem. Thermodyn. 8 (1976) 607–621.

[8] A.F. Bedford, A.E. Beezer, C.T. Mortimer, J. Chem. Soc., 1963, 2039-2043.

[9] V.P. Kolesov, S.M. Pimenova, V.A. Lukyanova, T.S. Kuznetsova, M.P. Kozina, J. Chem. Thermodyn. 30 (1998) 1455–1464.

[10] S.P. Verevkin, J. Chem. Thermodyn. 34 (2002) 263–275.

[11] W.V. Steele, R.D. Chirico, S.E. Knipmeyer, A. Nguyen, N.K. Smith, J. Chem. Eng. Data 41 (1996) 1285–1302.

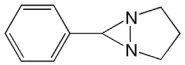
[12] S.P. Verevkin, V.N. Emel'yanenko, J. Phys. Chem. A 108 (2004) 6575–6580.

[13] A.F.L.O.M. Santos, M.A.V. Ribeiro da Silva, J. Chem. Thermodyn. 42 (2010) 734–741.

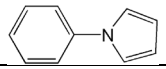
[14] A.B. Bazyleva, A.V. Blokhin, G.J. Kabo, M.B. Charapennikau, V.N. Emel'yanenko, S.P. Verevkin, V. Diky, J. Phys. Chem. B 115 (2011) 10064–10072.

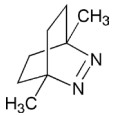
[15] D.H. Zaitsau, V.N. Emel'yanenko, A.A. Pimerzin, S.P. Verevkin, J. Chem. Thermodyn. 122 (2018) 1–12.

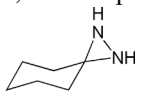
Table S5 Enthalpies of formation of PDABH and some related compounds calculated by DLPNO-CCSD(T_1)/CBS//B3LYP-D3(BJ)/def2-TZVPP and G4 methods using different working reactions (in kJ/mol at T=298.15 K)

Reactions for a given compound	Experiment		Calculation			
			DLPNO	Exp. – Calc.	G4	Exp. – Calc.
	$\Delta_f H^\circ_m$	Reference	$\Delta_f H^\circ_m$ [a]		$\Delta_f H^\circ_m$ [a]	
$C_{10}H_{12}N_2$ 6-Phenyl-1,5-diazabicyclo[3.1.0]hexane 						
Atomization reaction					334.1	
1 $C_{10}H_{12}N_2 + 6\ CH_4 \rightarrow 3\ C_2H_6 + 2\ C_2H_4 + C_6H_6 + NH_2NH_2$			343.6		327.0	
2 $C_{10}H_{12}N_2 + 6\ CH_4 \rightarrow 4\ C_2H_6 + C_2H_4 + C_6H_6 + NH{=}NH$			342.7		329.0	
3 $C_{10}H_{12}N_2 + 8\ CH_4 \rightarrow 4\ C_2H_6 + 2\ C_2H_4 + C_6H_6 + 2\ NH_3$			343.3		323.1	
4 $C_{10}H_{12}N_2 + 6\ CH_4 \rightarrow 2\ C_2H_6 + 2\ C_2H_4 + C_6H_6 + 2\ CH_3NH_2$			343.3		327.4	
5 $C_{10}H_{12}N_2 + 6\ CH_4 + CH_3C(O)CH_3 \rightarrow 4\ C_2H_6 + 2\ C_2H_4 + C_6H_6 + NH_2C(O)NH_2$			344.3		327.6	
6 $C_{10}H_{12}N_2 + C_3H_6$ (cyclopropane) $+ 2\ CH_4 \rightarrow 2\ C_2H_5N$ (aziridine) $+ C_5H_{10}$ (cyclopentane) $+ C_6H_6$			341.6		327.0	
7 $C_{10}H_{12}N_2 + 5\ CH_4 \rightarrow 3\ C_2H_6 + C_2H_4 + C_6H_6 + CH_4N_2$ (diaziridine)			342.9		329.0	
8 $C_{10}H_{12}N_2 + 5\ CH_4 \rightarrow 2\ C_2H_6 + 2\ C_2H_4 + C_6H_6 + CH_3NHNH_2$			343.5		329.8	
9 $C_{10}H_{12}N_2 + 4\ CH_4 \rightarrow C_2H_6 + 2\ C_2H_4 + C_6H_6 + (CH_3)_2NNH_2$			342.6		332.2	
10 $C_{10}H_{12}N_2 + 2\ CH_4 \rightarrow C_6H_{10}$ (bicyclo[3.1.0]hexane) $+ C_6H_6 + NH_2NH_2$			344.9		330.8	
11 $C_{10}H_{12}N_2 + CH_4 + C_2H_4 \rightarrow C_6H_{10}$ (bicyclo[3.1.0]hexane) $+ C_6H_6 + CH_4N_2$ (diaziridine)			344.2		332.8	
12 $C_{10}H_{12}N_2 + CH_4 + C_2H_6 \rightarrow C_6H_{10}$ (bicyclo[3.1.0]hexane) $+ C_6H_6 + CH_3NHNH_2$			344.8		333.6	
13 $C_{10}H_{12}N_2 + 2\ C_2H_6 \rightarrow C_6H_{10}$ (bicyclo[3.1.0]hexane) $+ C_6H_6 + (CH_3)_2NNH_2$			343.9		336.0	
14 $C_{10}H_{12}N_2 + C_6H_6 \rightarrow C_4H_8N_2$ (1,5-diazabicyclo[3.1.0]hexane) $+ C_6H_5{-}C_6H_5$			341.7		341.7	
Average of isodesmic-type reactions			343.4 ± 1.9		330.5 ± 6.8	
CH_4N_2 Diaziridine 						
Atomization reaction					236.0	
1 $CH_4N_2 + CH_4 \rightarrow NH_2NH_2 + C_2H_4$			236.1		233.3	
2 $CH_4N_2 + C_2H_6 \rightarrow NH_2NH_2 + C_3H_6$ (cyclopropane)			235.3		233.3	
3 $CH_4N_2 + CH_4 \rightarrow NH{=}NH + C_2H_6$			235.1		235.3	
4 $CH_4N_2 + C_2H_4 \rightarrow NH{=}NH + C_3H_6$ (cyclopropane)			234.4		235.3	
5 $CH_4N_2 + CH_2{=}CHCH_3 \rightarrow 2\ C_2H_5N$ (aziridine)			234.9		234.8	
6 $CH_4N_2 + C_3H_6$ (cyclopropane) $\rightarrow 2\ C_2H_5N$ (aziridine)			235.2		235.0	
7 $CH_4N_2 + C_2H_4O$ (oxirane) $\rightarrow NH_2C(O)NH_2 + C_2H_4$			235.6		232.3	

8	$CH_4N_2 + CH_3C(O)CH_3 \rightarrow NH_2C(O)NH_2 + C_3H_6$ (cyclopropane)			236.0		233.9	
9	$CH_4N_2 + 2\ CH_4 \rightarrow 2\ NH_3 + C3H_6$ (cyclopropane)			235.0		229.4	
10	$CH_4N_2 + 2\ CH_4 \rightarrow 2\ NH_3 + CH_2{=}CHCH_3$			235.3		229.6	
11	$CH_4N_2 + C_2H_6 \rightarrow CH_3NHNH_2 + C_2H_4$			235.9		236.1	
12	$CH_4N_2 + C_3H_8 \rightarrow CH_3NHNH_2 + C_3H_6$ (cyclopropane)			235.7		235.9	
13	$CH_4N_2 + C_3H_8 \rightarrow (CH_3)_2NNH_2 + C_2H_4$			235.6		238.2	
14	$CH_4N_2 + n\text{-}C_4H_{10} \rightarrow (CH_3)_2NNH_2 + C_3H_6$ (cyclopropane)			234.8		237.0	
	Average of isodesmic-type reactions			235.3 ± 1.0		234.2 ± 5.1	
$C_4H_8N_2$	1,5-Diazabicyclo[3.1.0]hexane						
							
	Atomization reaction					249.3	
1	$C_4H_8N_2 + 4\ CH_4 \rightarrow 2\ C_2H_6 + 2\ C_2H_4 + NH_2NH_2$			252.9		244.6	
2	$C_4H_8N_2 + 4\ CH_4 \rightarrow 3\ C_2H_6 + C_2H_4 + NH{=}NH$			251.9		246.6	
3	$C_4H_8N_2 + 6\ CH_4 \rightarrow 3\ C_2H_6 + 2\ C_2H_4 + 2\ NH_3$			252.6		240.7	
4	$C_4H_8N_2 + 4\ CH_4 \rightarrow C_2H_6 + 2\ C_2H_4 + 2\ CH_3NH_2$			252.5		245.0	
5	$C_4H_8N_2 + C_3H_6$ (cyclopropane) $+ C_2H_6 \rightarrow 2\ C_2H_5N$ (aziridine) $+ C_5H_{10}$ (cyclopentane)			250.9		244.6	
6	$C_4H_8N_2 + 3\ CH_4 \rightarrow 2\ C_2H_6 + C_2H_4 + CH_4N_2$ (diaziridine)			252.1		246.6	
7	$C_4H_8N_2 + C_2H_6 \rightarrow C_6H_{10}$ (bicyclo[3.1.0]hexane) $+ NH_2NH_2$			254.2		248.4	
8	$C_4H_8N_2 + 3\ CH_4 \rightarrow C_2H_6 + 2\ C_2H_4 + CH_3NHNH_2$			252.8		247.4	
9	$C_4H_8N_2 + 2\ CH_4 \rightarrow 2\ C_2H_4 + (CH_3)_2NNH_2$			251.9		249.8	
10	$C_4H_8N_2 + C_3H_8 \rightarrow C_6H_{10}$ (bicyclo[3.1.0]hexane) $+ CH_3NHNH_2$			254.6		251.0	
11	$C_4H_8N_2 + n\text{-}C_4H_{10} \rightarrow C_6H_{10}$ (bicyclo[3.1.0]hexane) $+ (CH_3)_2NNH_2$			253.6		252.2	
	Average of isodesmic-type reactions			252.7 ± 2.1		247.0 ± 6.6	
C_6H_{10}	Bicyclo[3.1.0]hexane	38.6 ± 2.1	[1]				
							
	Atomization reaction					37.9	0.7
1	$C_6H_{10} + 4\ CH_4 \rightarrow 3\ C_2H_6 + 2\ C_2H_4$			37.6	1.0	35.1	3.5
2	$C_6H_{10} + C_2H_6 \rightarrow C_5H_{10}$ (cyclopentane) $+ C_3H_6$ (cyclopropane)			35.7	2.9	33.3	5.3
3	$C_6H_{10} + C_2H_6 \rightarrow C_6H_{12}$ (cyclohexane) $+ C_2H_4$			35.8	2.8	35.7	2.9
	Average of isodesmic-type reactions			36.4 ± 2.2	2.2	34.7 ± 2.5	3.9

C_7H_{12} Norbornane	-53.6 ± 1.2 [2]					
						
Atomization reaction					-54.9	1.3
1 $C_6H_{10} + 4\ CH_4 \rightarrow 3\ C_2H_6 + 2\ C_2H_4$		-55.8	2.2	-58.4	4.8
2 $C_6H_{10} + C_2H_6 \rightarrow C_5H_{10}$ (cyclopentane) + C_3H_6 (cyclopropane)		-57.1	3.5	-58.0	4.4
3 $C_6H_{10} + C_2H_6 \rightarrow C_6H_{12}$ (cyclohexane) + C_2H_4		-56.4	2.8	-60.7	7.1
Average of isodesmic-type reactions		-56.4 ± 1.3	2.8	-59.1 ± 2.9	5.5
$C_{10}H_{16}$ Adamantane	-132.3 ± 2.2 [3]					
						
Atomization reaction					-139.5	7.2
1 $C_{10}H_{16} + 8\ CH_4 \rightarrow 6\ C_2H_6 + 3\ C_2H_4$		-133.5	1.2	-145.0	12.7
2 $C_{10}H_{16} + 2\ CH_4 \rightarrow 2\ C_6H_{12}$ (cyclohexane)		-131.9	-0.4	-143.2	10.9
3 $C_{10}H_{16} + C_3H_8 \rightarrow C_7H_{12}$ (norbornane) + C_6H_{12} (cyclohexane)		-133.0	0.7	-139.5	7.2
Average of isodesmic-type reactions		-132.8 ± 1.6	0.5	-142.6 ± 5.6	10.3
C_2H_5N Aziridine	126.7 ± 0.9 [4]					
						
Atomization reaction				127.5	-0.8	
1 $C_2H_5N + C_2H_6 \rightarrow CH_3NHCH_3 + C_2H_4$		125.7	1.0	127.0	-0.3	
2 $C_2H_5N + CH_4 \rightarrow CH_3NH_2 + C_2H_4$		127.4	-0.7	126.1	0.6	
3 $C_2H_5N + C_2H_6 \rightarrow CH_3CH_2NH_2 + C2H_4$		127.0	-0.3	126.0	0.7	
4 $C_2H_5N + CH_3OH + CH_4 \rightarrow C_2H_6 + NH_2OH + C_2H_4$		126.1	0.6	124.8	1.9	
5 $C_2H_5N + CH_3CH_2CH_3 \rightarrow CH_3NHCH_3 + C_3H_6$ (cyclopropane)		125.4	1.3	126.7	0.0	
6 $C_2H_5N + C_2H_6 \rightarrow CH_3NH_2 + C_3H_6$ (cyclopropane)		126.6	0.1	126.0	0.7	
7 $C_2H_5N + CH_3CH_2CH_3 \rightarrow CH_3CH_2NH_2 + C_3H_6$ (cyclopropane)		126.7	0.0	125.7	1.0	
8 $C_2H_5N + CH_4 \rightarrow C_3H_6$ (cyclopropane) + NH_3		126.6	0.1	123.9	2.8	
9 $C_2H_5N + CH_3NH_2 \rightarrow C_3H_6$ (cyclopropane) + NH_2NH_2		127.0	-0.3	125.6	1.1	
Average of isodesmic-type reactions		126.5 ± 1.2	0.2	125.8 ± 1.9	0.9	
$C_{10}H_9N$ 1-Phenylpyrrole	226.4 ± 2.4 [5]					
						

	Atomization reaction					222.7	3.7
1	$C_{10}H_9N + 10\ CH_4 \rightarrow 7\ C_2H_4 + 3\ C_2H_6 + NH_3$			228.3	-1.9	218.8	7.6
2	$C_{10}H_9N + 9\ CH_4 \rightarrow 7\ C_2H_4 + 2\ C_2H_6 + CH_3NH_2$			228.3	-1.9	220.9	5.5
3	$C_{10}H_9N + 8\ CH_4 \rightarrow 7\ C_2H_4 + C_2H_6 + CH_3NHCH_3$			226.6	-0.2	221.8	4.6
4	$C_{10}H_9N + 2\ CH_4 \rightarrow C_6H_6 + C_4H_5N$ (1H-pyrrole) $+ C_2H_6$			228.5	-2.1	221.3	5.1
	Average of isodesmic-type reactions			227.9 ± 1.8	-1.5	220.7 ± 2.7	5.7
$C_5H_8N_2$	2,3-Diazabicyclo[2.2.1]-hept-2-ene	207.4 ± 2.7	[6]				
							
	Atomization reaction					204.1	3.3
1	$C_5H_8N_2 + 7\ CH_4 \rightarrow 3\ C_2H_4 + 3\ C_2H_6 + 2\ NH_3$			207.7	-0.3	196.1	11.3
2	$C_5H_8N_2 + 5\ CH_4 \rightarrow 3\ C_2H_4 + 2\ C_2H_6 + NH_2NH_2$			208.0	-0.6	200.0	7.4
3	$C_5H_8N_2 + 5\ CH_4 \rightarrow 2\ C_2H_4 + 3\ C_2H_6 + NH{=}NH$			207.0	0.4	202.0	5.4
4	$C_5H_8N_2 + 5\ CH_4 \rightarrow 3\ C_2H_4 + C_2H_6 + 2\ CH_3NH_2$			207.6	-0.2	200.4	7.0
5	$C_5H_8N_2 + 4\ CH_4 \rightarrow 3\ C_2H_4 + C_2H_6 + CH_3NHNH_2$			207.8	-0.4	202.8	4.6
6	$C_5H_8N_2 + 3\ CH_4 \rightarrow 3\ C_2H_4 + (CH_3)_2NNH_2$			207.0	0.4	205.1	2.3
7	$C_5H_8N_2 + C_2H_6 \rightarrow C_7H_{12}$ (norbornane) $+ NH{=}NH$			208.7	-1.3	207.0	0.4
8	$C_5H_8N_2 + C_2H_6 \rightarrow C_7H_{10}$ (norbornene) $+ NH_2NH_2$			208.7	-1.3	204.4	3.0
9	$C_5H_8N_2 + C_3H_8 \rightarrow C_7H_{10}$ (norbornene) $+ CH_3NHNH_2$			209.1	-1.7	207.1	0.3
10	$C_5H_8N_2 + n\text{-}C_4H_{10} \rightarrow C_7H_{10}$ (norbornene) $+ (CH_3)_2NNH_2$			208.1	-0.7	208.2	-0.8
	Average of isodesmic-type reactions			208.0 ± 1.4	-0.6	203.3 ± 7.6	4.1
$C_8H_{14}N_2$	1,4-Dimethyl-2,3-diazabicyclo[2.2.2]octene-2	92.4 ± 4.4	[6]				
							
	Atomization reaction					78.1	14.3
1	$C_8H_{14}N_2 + 10\ CH_4 \rightarrow 3\ C_2H_4 + 6\ C_2H_6 + 2\ NH_3$			90.0	2.4	67.9	24.5
2	$C_8H_{14}N_2 + 8\ CH_4 \rightarrow 3\ C_2H_4 + 5\ C_2H_6 + NH_2NH_2$			90.4	2.0	71.8	20.6
3	$C_8H_{14}N_2 + 8\ CH_4 \rightarrow 2\ C_2H_4 + 6\ C_2H_6 + NH{=}NH$			89.4	3.0	73.8	18.6
4	$C_8H_{14}N_2 + 8\ CH_4 \rightarrow 3\ C_2H_4 + 4\ C_2H_6 + 2\ CH_3NH_2$			90.0	2.4	72.2	20.2
5	$C_8H_{14}N_2 + 7\ CH_4 \rightarrow 3\ C_2H_4 + 4\ C_2H_6 + CH_3NHNH_2$			90.2	2.2	74.6	17.8
6	$C_8H_{14}N_2 + 6\ CH_4 \rightarrow 3\ C_2H_4 + 3\ C_2H_6 + (CH_3)_2NNH_2$			89.3	3.1	76.9	15.5
7	$C_8H_{14}N_2 + 3\ CH_4 \rightarrow C_7H_{12}$ (norbornane) $+ NH{=}NH + 2\ C_2H_6$			91.1	1.3	78.8	13.6
8	$C_8H_{14}N_2 + 3\ CH_4 \rightarrow C_7H_{10}$ (norbornene) $+ NH_2NH_2 + 2\ C_2H_6$			91.0	1.4	76.3	16.1

9	$C_8H_{14}N_2 + 2\ CH_4 \rightarrow C_7H_{10}$ (norbornene) + $CH_3NHNH_2 + C_2H_6$			90.9	1.5	79.1	13.3
10	$C_8H_{14}N_2 + CH_4 \rightarrow C_7H_{10}$ (norbornene) + $(CH_3)_2NNH_2$			90.0	2.4	81.4	11.0
	Average of isodesmic-type reactions			90.2 ± 1.3	2.2	75.3 ± 8.1	17.1
$C_6H_{12}N_4$	Hexamethylenetetramine	203.7 ± 0.8	[7]				
							
	Atomization reaction					192.1	11.6
1	$C_6H_{12}N_4 + 12\ CH_4 \rightarrow 3\ C_2H_4 + 6\ C_2H_6 + 4\ NH_3$			202.2	1.5	175.0	28.7
2	$C_6H_{12}N_4 + 8\ CH_4 \rightarrow 3\ C_2H_4 + 4\ C_2H_6 + 2\ NH_2NH_2$			202.8	0.9	182.8	20.9
3	$C_6H_{12}N_4 + 8\ CH_4 \rightarrow C_2H_4 + 6\ C_2H_6 + 2$ NH=NH			200.9	2.8	186.8	16.9
4	$C_6H_{12}N_4 + 8\ CH_4 \rightarrow 3\ C_2H_4 + 2\ C_2H_6 + 4\ CH_3NH_2$			202.1	1.6	183.6	20.1
5	$C_6H_{12}N_4 + 6\ CH_4 \rightarrow 3\ C_2H_4 + 2\ C_2H_6 + 2\ CH_3NHNH_2$			202.5	1.2	188.4	15.3
6	$C_6H_{12}N_4 + 4\ CH_4 \rightarrow 3\ C_2H_4 + 2\ (CH_3)_2NNH_2$			200.8	2.9	193.0	10.7
7	$C_6H_{12}N_4 + 4\ C_6H_{12}$ (cyclohexane) $\rightarrow C_{10}H_{16}$ (adamantane) + 4 $C_5H_{11}N$ (piperidine)			202.4	1.3	202.8	0.9
	Average of isodesmic-type reactions			202.0 ± 1.6	1.7	187.5 ± 17.5	16.2
$C_6H_{12}N_2$	1,2-Diazaspiro[2.5]octane	128.5[b]	[8]				
							
	Atomization reaction					128.1	
1	$C_6H_{12}N_2 + 8\ CH_4 \rightarrow 2\ C_2H_4 + 5\ C_2H_6 + 2\ NH_3$			130.9		117.7	
2	$C_6H_{12}N_2 + 6\ CH_4 \rightarrow 2\ C_2H_4 + 4\ C_2H_6 + NH_2NH_2$			131.2		121.6	
3	$C_6H_{12}N_2 + 6\ CH_4 \rightarrow C_2H_4 + 5\ C_2H_6 +$ NH=NH			130.3		123.6	
4	$C_6H_{12}N_2 + 6\ CH_4 \rightarrow 2\ C_2H_4 + 3\ C_2H_6 + 2\ CH_3NH_2$			130.8		122.0	
5	$C_6H_{12}N_2 + 5\ CH_4 \rightarrow 2\ C_2H_4 + 3\ C_2H_6 + CH_3NHNH_2$			131.1		124.4	
6	$C_6H_{12}N_2 + 4\ CH_4 \rightarrow 2\ C_2H_4 + 2\ C_2H_6 + (CH_3)_2NNH_2$			130.2		126.7	
7	$C_6H_{12}N_2 + CH_4 \rightarrow C_6H_{12}$ (cyclohexane) + CH_4N_2 (diaziridine)			128.6		124.2	
8	$C_6H_{12}N_2 + C_2H_4 + C_2H_6 \rightarrow C_6H_{12}$ (cyclohexane) + 2 C_2H_5N (aziridine)			127.8		123.9	
9	$C_6H_{12}N_2 + CH_4 + C_2H_6 \rightarrow C_6H_{12}$ (cyclohexane) + C_3H_6 (cyclopropane) + NH_2NH_2			128.6		122.2	
10	$C_6H_{12}N_2 + 2\ CH_4 \rightarrow C_6H_{10}$ (bicyclo[3.1.0]hexane) + $N_2H_4 + C_2H_6$			132.5		125.4	
11	$C_6H_{12}N_2 + C_6H_6 + CH_4 \rightarrow C_4H_4N_2$ (pyrazine) + C_6H_{12} (cyclohexane) + C_3H_6 (cyclopropane)			126.1		124.4	
12	$C_6H_{12}N_2 + CH_4 \rightarrow C_4H_{10}N_2$ (piperazine) + C_3H_6 (cyclopropane)			127.5		125.2	
	Average of isodesmic-type reactions			129.6 ± 3.8		123.5 ± 4.7	

[a] The uncertainty of calculated values corresponds to twice the standard deviation of the mean.

[a] Result of high-level W1-F12 calculation.

References

[1] V.P. Kolesov, S.M. Pimenova, V.A. Lukyanova, T.S. Kuznetsova, M.P. Kozina, J. Chem. Thermodyn. 30 (1998) 1455–1464.

[2] S.P. Verevkin, V.N. Emel'yanenko, J. Phys. Chem. A 108 (2004) 6575–6580.

[3] A.B. Bazyleva, A.V. Blokhin, G.J. Kabo, M.B. Charapennikau, V.N. Emel'yanenko, S.P. Verevkin, V. Diky, J. Phys. Chem. B 115 (2011) 10064–10072.

[4] B. Ruscic, D.H. Bross, Active Thermochemical Tables (ATcT), Version 1.124: Argonne National Laboratory, 2022, http://atct.anl.gov/ (accessed May 25, 2023).

[5] A.F.L.O.M. Santos, M.A.V. Ribeiro da Silva, J. Chem. Thermodyn. 42 (2010) 734–741.

[6] P.S. Engel, R.A. Melaugh, M. Månsson, J. W. Timberlake, A.W. Garner, F.D. Rossini, J. Chem. Thermodyn. 8 (1976) 607–621.

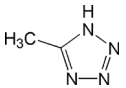
[7] S.P. Verevkin, J. Chem. Thermodyn. 34 (2002) 263–275.

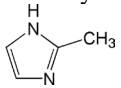
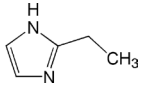
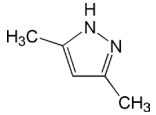
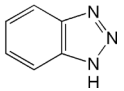
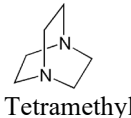
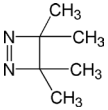
[8] N.V. Muravyev, K.A. Monogarov, I.N. Melnikov, A.N. Pivkina, V.G. Kiselev, Phys. Chem. Chem. Phys. 23 (2021) 15522–15542.

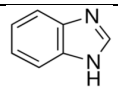
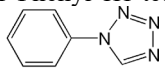
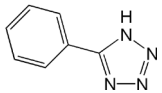
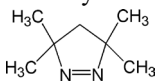
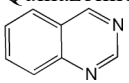
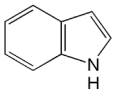
Table S6 Molecular electrostatic potential parameters calculated for the molecular geometries optimized at the B3LYP/6-311++G(3df,2p) level and coefficients *a*, *b*, *c*, *d*, *e* and *f* in the equation relating the enthalpy of sublimation to the descriptors of electrostatic potential. Comparison between experimental and calculated enthalpies of sublimation

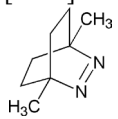
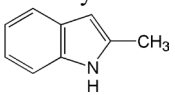
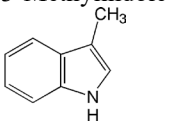
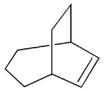
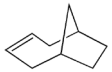
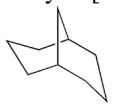
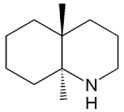
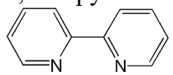
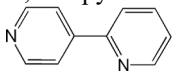
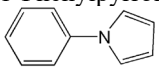
$$\Delta_{\mathrm{sub}}H^{\circ}_{\mathrm{m}}(298.15\ \mathrm{K}) = a\rho + bA_{\mathrm{S}} + c\overline{V}_{\mathrm{S}} + d(\sigma^2_{\mathrm{tot}}v) + e\Pi + f$$

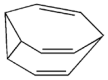
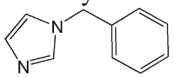
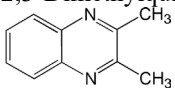
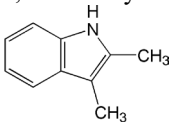
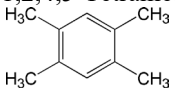
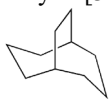
a = 8.080614 kcal·mol^{-1}·cm^3·g^{-1}
b = 0.100881 kcal·mol^{-1}·Å^{-2}
c = -0.454822
d = 0.139893 (kcal·mol^{-1})$^{-1}$
e = 0.254010
f = -13.949259 kcal·mol^{-1}

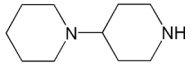
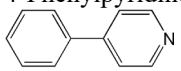
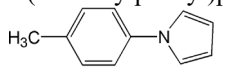
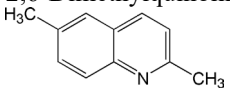
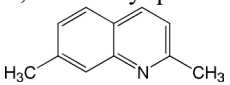
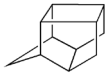
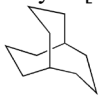
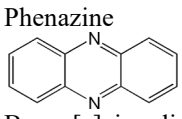
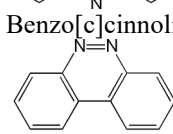
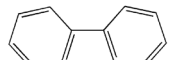
	Molecule		$\Delta_{\mathrm{sub}}H^{\circ}_{\mathrm{m}}$(exp) kJ·mol^{-1}	Reference [a]	$\Delta_{\mathrm{sub}}H^{\circ}_{\mathrm{m}}$(calc) kJ·mol^{-1}	Δ [b] kJ·mol^{-1}	ρ g·cm^{-3}	A_{S} Å^2	$\overline{V}_{\mathrm{S}}$ kcal·mol^{-1}	$\sigma^2_{\mathrm{tot}}v$ (kcal·mol^{-1})^2	Π kcal·mol^{-1}
1	CH_2N_4	1*H*-Tetrazole 	90.1 ± 1.6	[1]: 1990KOZ/SIM	93.8	-3.7	1.4399	95.34080	2.15423	70.84512	24.32154
2	$C_2H_3N_3$	1*H*-1,2,4-Triazole 	84.0 ± 0.7	[1]: 1989JIM/ROU	82.7	1.3	1.3332	100.09657	1.54833	65.94989	17.06130
3	$C_2H_4N_4$	5-Methyl-1*H*-tetrazole 	96.3 ± 0.5	[1]: 1990KOZ/SIM	94.0	2.3	1.3404	117.98407	2.96497	66.56570	22.51817
4	$C_3H_3N_3$	1,3,5-Triazine 	54.2 ± 0.2	[1]: 1982BYS	53.0	1.2	1.3516	112.02979	2.36439	18.44257	11.37348
5	$C_3H_4N_2$	1*H*-Imidazole 	83.1 ± 0.2	[1]: 1987JIM/ROU	88.3	-5.2	1.2255	105.31562	1.10623	77.39458	16.51049
6	$C_3H_4N_2$	1*H*-Pyrazole 	72.6 ± 0.8	[2]	71.1	1.5	1.2220	105.28471	1.03638	52.68342	13.97204
7	$C_4H_4N_2$	Pyrazine	57.5 ± 0.4	[1]: 2012VER/EME	55.7	1.8	1.2535	117.10627	1.78826	24.86566	10.40565

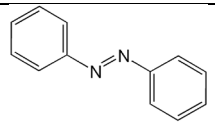
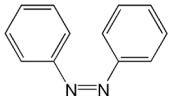
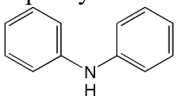
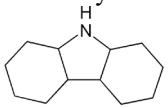
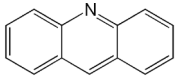
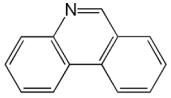
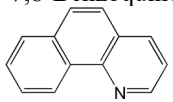
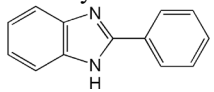
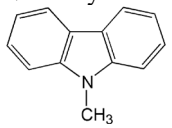
8	$C_4H_6N_2$	 2-Methylimidazole	88.4 ± 0.7	[1]: 1992JIM/ROU	86.5	1.9	1.1786	127.58189	1.04881	64.95114	14.22767
9	$C_5H_8N_2$	 2-Ethylimidazole	89.6 ± 0.4	[1]: 1992JIM/ROU	90.1	-0.5	1.1485	148.04752	0.75129	60.60051	12.28993
10	$C_5H_8N_2$	 3,5-Dimethylpyrazole	83.4 ± 2.4	[1]: 2001RIB/FER	78.7	4.7	1.1459	149.57644	0.87113	42.71403	11.18598
11	$C_5H_8N_2$	 2,3-Diazabicyclo[2.2.1]-hept-2-ene	55.3 ± 0.6	[1]: 1976ENG/MEL	57.1	-1.8	1.2165	135.54804	2.35346	14.40614	12.38346
12	$C_6H_5N_3$	 1*H*-Benzotriazole	99.0 ± 0.5	[1]: 1989JIM/ROU	102.1	-3.1	1.3499	150.21462	1.73021	67.81589	14.11554
13	C_6H_6	 Benzene	44.7 ± 0.2	[3]	43.6	1.1	1.0913	126.52514	0.75830	8.364760	7.69947
14	$C_6H_{12}N_2$	 1,4-Diazabicyclo[2.2.2]octane	61.9 ± 3.3	[1]: 1960WAD/KIS	54.9	7.0	1.1682	155.02170	1.96605	7.018490	7.50366
15	$C_6H_{12}N_2$	 Tetramethyldiazetine	62.3 ± 0.3	[1]: 1978MON/ENG	64.8	-2.5	1.0869	167.96108	2.48581	15.30462	10.61700
16	$C_6H_{12}N_4$	 Hexamethylenetetramine	79.6 ± 0.4	[1]: 2002VER2	68.9	10.7	1.3235	162.69942	1.92728	13.14574	9.245210
17	$C_7H_6N_2$	 1*H*-Benzimidazole	102.2 ± 0.4	[1]: 1987JIM/ROU	97.6	4.6	1.2908	154.68820	0.58525	57.70676	13.54857

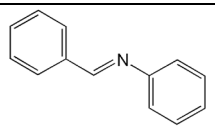
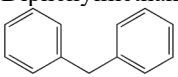
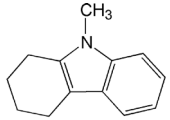
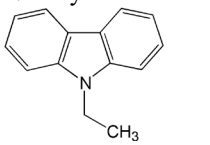
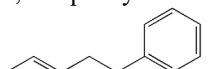
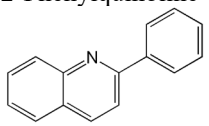
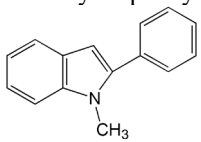
18	$C_7H_6N_4$	 1-Phenyl-1*H*-tetrazole	104.0 ± 3.0	[4]	101.7	2.3	1.3557	178.59656	3.18704	49.42998	15.03911
19	$C_7H_6N_4$	 5-Phenyl-1*H*-tetrazole	115.0 ± 3.0	[4]	119.2	-4.2	1.3573	177.88138	2.92513	78.02811	15.47864
20	C_7H_{10}	 2-Norbornene	37.7 ± 0.9	[1]: 1978STE2	43.3	-5.6	1.0955	144.28742	1.53389	4.775550	3.57352
21	C_7H_{10}	 Nortricyclene	39.2 ± 1.1	[1]: 1976KOZ/BYC	41.9	-2.7	1.1240	141.65071	1.38551	3.046210	3.08917
22	C_7H_{12}	 Norbornane	40.1 ± 0.4	[1]: 2004VER/EME	39.8	0.3	1.0653	149.37874	1.87868	0.443250	2.31321
23	$C_7H_{14}N_2$	 1,1,3,3-Tetramethyl-trimethylenediazene	61.6 ± 0.2	[1]: 1976ENG/MEL	70.0	-8.3	1.0819	185.8329	2.04328	13.41022	8.81165
24	$C_8H_6N_2$	 Quinazoline	76.6 ± 1.4	[1]: 1995RIB/MAT4	80.4	-3.8	1.3025	165.12251	1.56166	29.68440	9.95365
25	C_8H_7N	 1*H*-Indole	73.9 ± 0.4	[1]: 2011VER/EME3	75.8	-1.9	1.2280	159.48564	0.27046	24.55837	10.81636
26	C_8H_{12}	 Bicyclo[2.2.2]oct-2-ene	43.8 ± 0.1	[1]: 1971WON/WES	48.5	-4.7	1.1005	158.98000	1.62031	3.785010	3.22674
27	C_8H_{14}	 Bicyclo[2.2.2]octane	48.0 ± 0.2	[1]: 1971WON/WES	45.7	2.3	1.0726	163.88460	2.02160	0.495070	2.04995
28	$C_8H_{14}N_2$	 1,4-Dimethyl-2,3-diazabicyclo-									

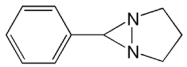
		[2.2.2]octene-2 	72.0 ± 0.5	[1]: 1976ENG/MEL	74.0	-2.0	1.1584	185.63733	2.02040	15.09774	9.27705
29	C_9H_9N	2-Methylindole 	86.0 ± 0.3	[5]	83.8	2.2	1.1985	181.22812	0.56723	25.49906	10.66127
30	C_9H_9N	3-Methylindole 	90.4 ± 1.9	[1]: 2009RIB/CAB2	82.1	8.3	1.1989	179.56843	0.28543	24.97758	9.46616
31	C_9H_{14}	Bicyclo[3.2.2]non-6-ene 	48.0 ± 1.0	[1]: 1983JOC/DEK2	53.8	-5.8	1.1002	172.83933	1.70136	3.483650	3.01007
32	C_9H_{14}	Bicyclo[4.2.1]non-3-ene 	49.7 ± 0.8	[1]: 1983JOC/DEK2	54.5	-4.8	1.0888	175.25385	1.64657	3.041050	3.20774
33	C_9H_{16}	Bicyclo[3.3.1]nonane 	50.6 ± 2.1	[1]: 1977PAR/STE	51.3	-0.7	1.0758	177.38859	2.03476	0.441030	1.86747
34	$C_9H_{17}N$	*trans*-Decahydroquinoline 	77.9	[1]: 1994STE/CHI	67.2	10.7	1.0951	195.13565	1.71043	9.529910	3.64767
35	$C_{10}H_8N_2$	2,2'-Bipyridine 	81.8 ± 2.3	[1]: 1995RIB/MOR	86.7	-4.9	1.2759	197.78770	-0.22872	14.66943	8.83875
36	$C_{10}H_8N_2$	2,4'-Bipyridine 	87.9 ± 1.7	[1]: 1995RIB/MOR	94.4	-6.5	1.2754	197.47897	1.21630	30.20946	10.25184
37	$C_{10}H_9N$	1-Phenylpyrrole 	80.8 ± 0.6	[1]: 2010SAN/RIB	78.3	2.5	1.2089	191.65672	0.93854	13.23911	8.38267
38	$C_{10}H_{10}$	Basketene	55.3 ± 0.5	[1]: 2002VER/KUM	58.9	-3.6	1.2561	167.03375	1.23442	4.53104	3.75702

39	$C_{10}H_{10}$	 Snoutene	58.7 ± 0.4	[1]: 2002VER/KUM	60.9	-2.2	1.2598	165.28981	0.88181	5.19876	5.20359
40	$C_{10}H_{10}$	 Bullvalene	71.8 ± 0.4	[1]: 1981MAN/SUN	66.7	5.1	1.1965	171.14981	0.65769	9.56828	7.58814
41	$C_{10}H_{10}N_2$	 1-Benzylimidazole	102.1 ± 0.4	[1]: 1999MO/YAN	96.9	5.2	1.2250	208.44063	2.17577	30.50270	11.4798
42	$C_{10}H_{10}N_2$	 2,3-Dimethylquinoxaline	85.8 ± 1.8	[1]: 1996RIB/MOR	86.3	-0.5	1.2401	204.14497	0.43877	13.88562	8.73916
43	$C_{10}H_{11}N$	 2,3-Dimethylindole	86.8 ± 0.3	[1]: 2011VER/EME3	89.4	-2.6	1.1803	198.64452	0.57752	25.71572	9.44185
44	$C_{10}H_{14}$	 1,2,4,5-Tetramethylbenzene	74.6 ± 0.3	[1]: 1989COL/JIM	70.7	3.9	1.0644	201.25780	0.81863	7.02784	5.23709
45	$C_{10}H_{16}$	 Adamantane	59.1 ± 0.9	[1]: 2011BAS/BLO	54.4	4.7	1.1392	179.83445	2.02888	0.44449	1.86013
46	$C_{10}H_{16}$	 *endo*-Tricyclo[5.2.1.0(2.6)]-decane	52.9 ± 1.3	[1]: 1971BOY/SAN	56.2	-3.3	1.1278	183.50775	1.91733	0.43618	2.20134
47	$C_{10}H_{18}$	 Bicyclo[3.3.2]decane	58.2 ± 2.1	[1]: 1977PAR/STE	56.6	1.6	1.0789	189.93903	2.09483	0.50922	1.88924
48	$C_{10}H_{20}N_2$	 4-Piperidinopiperidine	88.6 ± 1.9	[6]	83.9	4.7	1.1139	227.81089	1.35802	10.96802	4.35949

49	$C_{11}H_9N$	 4-Phenylpyridine	81.4 ± 1.6	[7]: 2000RIB/MAT2	86.4	-5.0	1.2275	201.96303	1.57253	19.50499	8.97987
50	$C_{11}H_{11}N$	 1-(4-Methylphenyl)pyrrole	83.7 ± 0.5	[8]	85.3	-1.6	1.1872	212.49863	1.00524	12.04399	8.19349
51	$C_{11}H_{11}N$	 2,6-Dimethylquinoline	84.5 ± 1.5	[7]: 1995RIB/MAT3	87.7	-3.2	1.1941	211.32864	0.35097	14.25110	8.29110
52	$C_{11}H_{11}N$	 2,7-Dimethylquinoline	87.5 ± 1.5	[7]: 1995RIB/MAT3	88.0	-0.5	1.1939	211.34422	0.21046	14.50330	8.17975
53	$C_{11}H_{14}$	 Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecane	55.9 ± 1.0	[7]: 1995KAB/KOZ	59.3	-3.5	1.2371	181.29294	1.66853	0.43389	2.14808
54	$C_{11}H_{20}$	 Bicyclo[3.3.3]undecane	63.6 ± 0.8	[7]: 1975PAR/STE	61.7	1.9	1.0831	201.79329	2.08992	0.48277	1.83049
55	$C_{12}H_8N_2$	 Phenazine	95.9 ± 0.4	[7]: 2010CHI/KAZ2	94.8	1.1	1.3232	213.80519	0.09269	16.44519	8.24455
56	$C_{12}H_8N_2$	 Benzo[c]cinnoline	103.0 ± 0.6	[9]	102.9	0.1	1.3271	210.66074	0.96408	31.14264	10.44282
57	$C_{12}H_9N$	 Carbazole	103.3 ± 1.1	[7]: 1990JIM/ROU	92.2	11.1	1.2736	207.29059	0.52652	18.04690	9.87240
58	$C_{12}H_{10}$	 Biphenyl	81.8 ± 0.2	[10]	80.7	1.1	1.1838	206.46788	0.46088	7.84219	7.70053
59	$C_{12}H_{10}N_2$	*trans*-Azobenzene	94.1 ± 0.7	[7]: 1996STE/CHI2	96.7	-2.6	1.2426	234.79872	-0.24007	8.48688	8.03450

											
60	$C_{12}H_{10}N_2$	*cis*-Azobenzene	92.9 ± 0.1	[7]: 1977SHU/PET	98.8	-5.9	1.2481	228.90069	0.92741	17.33193	9.42839
											
61	$C_{12}H_{11}N$	Diphenylamine	95.2 ± 0.6	[7]: 2011SUR/PER	91.8	3.4	1.2076	221.59530	0.83273	14.16766	8.54839
											
62	$C_{12}H_{21}N$	Dodecahydrocarbazole	84.0 ± 0.6	[7]: 2015STA/EME	84.3	-0.3	1.1289	233.76395	1.76683	8.69866	3.81675
											
63	$C_{13}H_9N$	Acridine	94.5 ± 4.0	[7]: 1989STE/CHI	95.7	-1.2	1.2819	217.49444	0.21875	16.76061	8.97737
											
64	$C_{13}H_9N$	Phenanthridine	98.6 ± 4.0	[7]: 1989STE/CHI	95.1	3.5	1.2891	214.34748	0.60818	18.6712	9.10132
											
65	$C_{13}H_9N$	7,8-Benzoquinoline	90.2 ± 2.0	[7]: 1989STE/CHI	93.7	-3.5	1.2888	214.77928	0.04126	14.44425	8.88206
											
66	$C_{13}H_{10}N_2$	2-Phenylbenzimidazole	123.0 ± 1.7	[7]: 2005RIB/RIB	115.6	7.4	1.2917	236.08684	0.49833	34.50155	10.71882
											
67	$C_{13}H_{11}N$	*N*-Methylcarbazole	92.7 ± 1.9	[11]	95.2	-2.5	1.2508	224.11769	0.56080	13.19238	9.45143
											
68	$C_{13}H_{11}N$	(*N*-Phenylmethylene)-benzenamine	98.1 ± 1.2	[7]: 1997VER/MOR	99.0	-0.9	1.2067	239.27696	0.27102	12.19333	8.43134

69	$C_{13}H_{12}$	 Diphenylmethane	87.6 ± 0.8	[7]: 1999VER5	88.6	-1.4	1.1620	227.68910	0.51746	7.97693	7.45543
70	$C_{13}H_{15}N$	 1,2,3,4-Tetrahydro-*N*-methylcarbazole	93.5 ± 1.4	[11]	97.9	-4.4	1.2013	235.92084	0.75491	14.63471	8.37394
71	$C_{14}H_{13}N$	 *N*-Ethylcarbazole	97.1 ± 1.0	[7]: 2011VER/EME	100.9	-3.8	1.2276	242.76036	0.7224	12.17591	9.02055
72	$C_{14}H_{14}$	 1,2-Diphenylethane	93.2 ± 0.9	[7]: 2001MON/HIL5	96.7	-3.5	1.1446	250.13337	1.10675	8.67195	7.32091
73	$C_{14}H_{24}$	 *trans-syn-trans*-Tetradeca-hydroanthracene	87.4 ± 2.4	[7]: 1963MAR/FRI	84.1	3.3	1.0957	253.54389	2.09481	0.61615	1.92468
74	$C_{15}H_{11}N$	 2-Phenylquinoline	105.4 ± 0.9	[7]: 1997RIB/MAT3	107.2	-1.8	1.2650	249.65384	-0.05865	13.93466	8.64297
75	$C_{15}H_{13}N$	 1-Methyl-2-phenylindole	111.1 ± 0.7	[12]	107.3	3.8	1.2359	256.15678	0.63844	12.99293	8.80301
				Root-mean-square deviation:		**4.2 kJ·mol^{-1}**					
				Maximum deviation:		11.1 kJ·mol^{-1}					
				Minimum deviation:		-8.3 kJ·mol^{-1}					

$C_{10}H_{12}N_2$	6-Phenyl-1,5-diazabicyclo[3.1.0]hexane 	**92.9**	1.2165	210.79916	0.31218	17.13877	10.98777

[a] References to the experimental data for most of the compounds are given in the compendium by Acree and Chickos [1,7]; for these compounds, in addition to Refs. [1,7], the corresponding references from this compendium are given nearby. The list of all references is given below.
[b] $\Delta = \Delta_{\mathrm{sub}}H^{\circ}_{\mathrm{m}}(298.15\ \mathrm{K},\ \mathrm{exp}) - \Delta_{\mathrm{sub}}H^{\circ}_{\mathrm{m}}(298.15\ \mathrm{K},\ \mathrm{calc})$.

References

[1] W. Acree, Jr., J.S. Chickos, J. Phys. Chem. Ref. Data 45 (2016) 033101.

[2] S.P. Safronov, R.N. Nagrimanov, A.A. Samatov, V.N. Emel'yanenko, D.H. Zaitsau, A.A. Pimerzin, A. Skrzypczak, S.P. Verevkin, J. Chem. Thermodyn. 128 (2019) 173–186.

[3] M.J.S. Monte, A.R.R.P. Almeida, Struct. Chem. 24 (2013) 2001–2016.

[4] A.A. Balepin, V.P. Lebedev, E.A. Miroshnichenko, G.I. Koldobskii, V.A. Ostovskii, B.P. Larionov, B.V. Gidaspov, Yu.A. Lebedev, Svoistva Veshchestv Str. Mol., 1977, 93-98 (cited from NIST Chemistry WebBook, http://webbook.nist.gov/chemistry/).

[5] R.D. Chirico, E. Paulechka, A. Bazyleva, A.F. Kazakov, J. Chem. Thermodyn. 125 (2018) 257–270.

[6] M.A.V. Ribeiro da Silva, J.I.T.A. Cabral, J. Therm. Anal. Calorim. 90 (2007) 865–871.

[7] W. Acree, Jr., J.S. Chickos, J. Phys. Chem. Ref. Data 46 (2017) 013104.

[8] A.F.L.O.M. Santos, M.A.V. Ribeiro da Silva, J. Chem. Thermodyn. 42 (2010) 734–741.

[9] H.K. Cammenga, V.N. Emel'yanenko, S.P. Verevkin, Ind. Eng. Chem. Res. 48 (2009) 10120–10128.

[10] D.H. Zaitsau, V.N. Emel'yanenko, A.A. Pimerzin, S.P. Verevkin, J. Chem. Thermodyn. 122 (2018) 1–12.

[11] K. Stark, V.N. Emel'yanenko, A.A. Zhabina, M.A. Varfolomeev, S.P. Verevkin, K. Müller, W. Arlt, Ind. Eng. Chem. Res. 54 (2015) 7953−7966.

[12] T.M.T. Carvalho, L.M.P.F. Amaral, V.M.F. Morais, M.D.M.C. Ribeiro da Silva, J. Chem. Thermodyn. 85 (2015) 129–140.

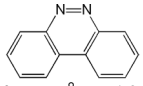
Table S7 Estimation of enthalpy of formation of PDABH by comparison with related compounds

1. Estimation of $\Delta_{sub}H^{\circ}_{m}$(298.15 K) value for bicyclo[3.1.0]hexane using group additivity method of Naef and Acree [1][a]

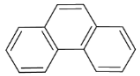
$\Delta_{sub}H^{\circ}_{m}$(bicyclo[3.1.0]hexane) = 4 [H2C2] + 2 [HC3] + C = 4·6.88 + 2·2.28 + 21.03 = 53.1 kJ·mol^{-1}

2. Estimation of correction in the sublimation enthalpy at 298.15 K when the cyclic C–C bond is replaced by cyclic N–N bond

$\Delta_1 = \Delta_{sub}H^{\circ}_{m}(\mathrm{N-N}) - \Delta_{sub}H^{\circ}_{m}(\mathrm{C-C})$



$\Delta_{sub}H^{\circ}_{m}$ = 103.0 ± 0.6 kJ·mol^{-1} [2]



$\Delta_{sub}H^{\circ}_{m}$ = 89.6 ± 0.8 kJ·mol^{-1} [2] 13.4 kJ·mol^{-1}

$\Delta_{sub}H^{\circ}_{m}$ = 55.3 ± 0.6 kJ·mol^{-1} [3]

$\Delta_{sub}H^{\circ}_{m}$ = 37.7 ± 0.9 kJ·mol^{-1} [4] 17.6 kJ·mol^{-1}

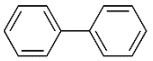
$\Delta_{sub}H^{\circ}_{m}$ = 55.3 ± 0.6 kJ·mol^{-1} [3]

$\Delta_{sub}H^{\circ}_{m}$ = 40.1 ± 0.4 kJ·mol^{-1} [5] 15.2 kJ·mol^{-1}

average Δ_1 15.4 kJ·mol^{-1}

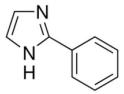
2. Estimation of correction in the sublimation enthalpy when the C–H bond is replaced by benzene ring

$\Delta_2 = \Delta_{sub}H^{\circ}_{m}(\mathrm{C-C_6H_5}) - \Delta_{sub}H^{\circ}_{m}(\mathrm{C-H})$



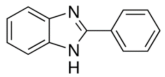
$\Delta_{sub}H^{\circ}_{m}$ = 81.8 ± 0.2 kJ·mol^{-1} [6]

$\Delta_{sub}H^{\circ}_{m}$ = 46.6 ± 0.4 kJ·mol^{-1} [7] 35.2 kJ·mol^{-1}



$\Delta_{sub}H^{\circ}_{m}$ = 113.6 ± 0.6 kJ·mol^{-1} [8]

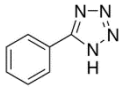
$\Delta_{sub}H^{\circ}_{m}$ = 83.1 ± 0.2 kJ·mol^{-1} [9] 30.5 kJ·mol^{-1}



$\Delta_{sub}H^{\circ}_{m}$ = 123.0 ± 1.7 kJ·mol^{-1} [10]

$\Delta_{sub}H^{\circ}_{m}$ = 102.2 ± 0.4 kJ·mol^{-1} [9]

20.8 kJ·mol^{-1}



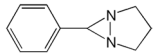
$\Delta_{sub}H^{\circ}_{m}$ = 115.0 ± 3.0 kJ·mol^{-1} [11]

$\Delta_{sub}H^{\circ}_{m}$ = 90.1 ± 1.6 kJ·mol^{-1} [12]

24.9 kJ·mol^{-1}

average Δ_2 27.9 kJ·mol^{-1}

3. Estimation of $\Delta_{sub}H^{\circ}_{m}$(298.15 K) value for PDABH



$\Delta_{sub}H^{\circ}_{m}$(PDABH) = $\Delta_{sub}H^{\circ}_{m}$(bicyclo[3.1.0]hexane) + Δ_1 + Δ_2 = 53.1 + 15.4 + 27.9 = **96.4 kJ·mol^{-1}**

[a] Bicyclo[3.1.0]hexane is the liquid compound. Its enthalpy of vaporization estimated using the group contribution values by Naef and Acree [1] gives the value of 34.4 kJ·mol^{-1} in good agreement with the experimental value (33.5 ± 0.4 kJ·mol^{-1} [13]); to estimate the enthalpy of sublimation, the corresponding group contributions for the enthalpy of sublimation were used.

References

[1] R. Naef, W.E. Acree Jr., Molecules 22 (2017) 1059.

[2] H.K. Cammenga, V.N. Emel'yanenko, S.P. Verevkin, Ind. Eng. Chem. Res. 48 (2009) 10120–10128.

[3] P.S. Engel, R.A. Melaugh, M. Månsson, J. W. Timberlake, A.W. Garner, F.D. Rossini, J. Chem. Thermodyn. 8 (1976) 607–621.

[4] W.V. Steele, J. Chem. Thermodyn. 10 (1978) 919–927.

[5] S.P. Verevkin, V.N. Emel'yanenko, J. Phys. Chem. A 108 (2004) 6575–6580.

[6] D.H. Zaitsau, V.N. Emel'yanenko, A.A. Pimerzin, S.P. Verevkin, J. Chem. Thermodyn. 122 (2018) 1–12.

[7] M.J.S. Monte, A.R.R.P. Almeida, Struct. Chem. 24 (2013) 2001–2016.

[8] L. Infantes, O. Mó, M. Yáñez, M.V. Roux, P. Jiménez, J.Z. Dávalos, M. Temprado, M.A.V. Ribeiro da Silva, M.D.M.C. Ribeiro da Silva, L.M.P.F. Amaral, P. Cabildo, R. Claramunt, J. Elguero, J. Phys. Chem. A 110 (2006) 2535–2544.

[9] P. Jiménez, M.V. Roux, C. Turrión, F. Gomis, J. Chem. Thermodyn. 19 (1987) 985–992.

[10] M.A.V. Ribeiro da Silva, M.D.M.C. Ribeiro da Silva, L.M.P.F. Amaral, J. Elguero, P. Jiménez, M.V. Roux, J.Z. Dávalos, M. Temprado, P. Cabildo, R.M. Claramunt, O. Mó, M. Yáñez, J. Chem. Thermodyn. 37 (2005) 1168-1176.

[11] A.A. Balepin, V.P. Lebedev, E.A. Miroshnichenko, G.I. Koldobskii, V.A. Ostovskii, B.P. Larionov, B.V. Gidaspov, Yu.A. Lebedev, Svoistva Veshchestv Str. Mol., 1977, 93-98 (cited from NIST Chemistry WebBook, http://webbook.nist.gov/chemistry/).

[12] A.A. Kozyro, V.V. Simirskii, G.Ya. Kabo, M.L. Frenkel, A.P. Krasulin, V.M. Sevruk, N.A. Sokolov, Russ. J. Phys. Chem. 64 (1990) 1274-1275.

[13] S. Chang, D. McNally, S. Shary-Tehrany, S.M.J. Hickey, R.H. Boyd, J. Am. Chem. Soc. 92 (1970) 3109–3118.