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Molecular structure of 3,3-pentamethylenediaziridine in gas and solution phases

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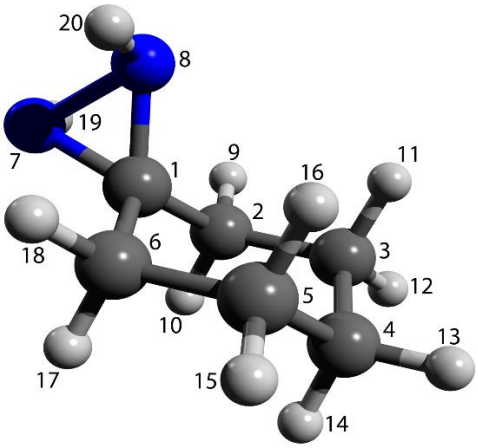

Figure S1. Molecular model of 3,3-pentamethylenediaziridine (PMDA). Atom numbering and coloring: (blue) nitrogen, (dark grey) carbon, and (light grey) hydrogen.

1. Methodical: Synthesis and measurements

1.1 Synthesis of 3,3-pentamethylenediaziridine (PMDA)

3,3-Pentamethylenediaziridine (PMDA) was synthesized according to the procedure given in Ref. S1. All starting materials were purchased from commercial sources. A solution of 14.7 g (0.15 moles) of cyclohexanone in 40 ml of 15N aqueous ammonia (0.6 moles) in a 0.1-l beaker was stirred mechanically and cooled to 0°C with an ice-salt mixture. Maintaining the temperature of the solution between 0° and +10°C, 12.4 g (0.1 mole) of 90% hydroxylamine-O-sulfonic acid was added in portions of about 0.1 g. The addition has taken about half an hour, and the mixture was stirred for another hour at 0°C and allowed to stand overnight at −15°C in a freezer. The precipitated crystalline cake was filtered and pressed tightly with a glass stopper. The solid was washed with 10-ml portions of ice-cold ether, toluene, and finally ether. There was obtained 11.0–11.5 g of product which was ~70% pure (iodometric titration). The product was divided into two portions, each of which was boiled shortly with a 10-ml portion of toluene; the solutions were decanted from small salt residues and cooled to 0°C for 2 hours. The precipitates were filtered with suction and washed with 20 ml of ice-cold petroleum ether. The combined yield of 3,3-pentamethylenediaziridine was 6.8–7.8 g (61–70%), m.p. 104–107°. The purity was 96–100% (iodometric titration).

1.2 Analytical measurements

NMR spectra were recorded on Bruker Avance 400 spectrometers: ^{1}H NMR spectra at temperatures, K: 298, 302, and 323 ; ^{13}C NMR spectra at 283 K; {^{1}H-^{13}C}HSQC spectra at 298 and 273 K; {^{1}H-^{13}C}HMBC spectra at 263 K; {^{1}H–^{1}H}gNOESY spectra at 298 and 278 K. The chemical shifts δ were measured in ppm with respect to solvent ($CDCl_3$: ^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.0 ppm). Splitting patterns are denoted as *s* for singlet; *d* for doublet; *t* for triplet; *q* for quartet; *m* for multiplet; and *dt* for doublet triplet. The structures of synthesized compounds were elucidated with the use of 1D NMR (^{1}H, ^{13}C) and 2D NMR (HSQC and HMBC ^{1}H-^{13}C, NOESY ^{1}H-^{1}H) spectroscopy. The IR spectra were recorded on Bruker "Alpha" spectrometers in a range of 400-4000 cm^{-1} (at a resolution of 2 cm^{-1}). High-resolution mass spectra were recorded on a Bruker microTOF-QTM spectrometer with electrospray ionization (ESI). All measurements were performed in a positive (+MS) ion mode (interface capillary voltage: 4500 V) in a 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 points (mp) were determined using Electrothermal 9100 and SMP-20 capillary melting

point apparatus. Column chromatography was performed on silica gel 60 (230-400 mesh, Merck or Macherey-Nagel).

1.3 Characterization

^{1}H NMR ($CDCl_3$, 400.16 MHz, 298 K): δ = 1.35-1.42 (dt, 2 H, H − 13,14), 1.42-1.68 (m, 8 H, H – 9,10,11,12,15,16,17,18,19,20). ^{13}C NMR ($CDCl_3$, 100.62 MHz, 283 K): δ = 24.7 C (3), C(5), 24.8 C(4), 35.9 C (2), C(6), 57.4 C (1).

IR (KBr): ν = 3445, 3180, 2932, 2895, 2854, 2652, 2597, 2547, 2514, 2303, 2243, 1638, 1446, 1406, 1367, 1337, 1315, 1257, 1218, 1202, 1141, 1111, 1072, 1046, 930, 889, 836, 783, 668, 552, 468, 432 cm^{-1}.

HRMS (ESI-TOF): m/z calcd. for $C_6H_{12}N_2^+$: 113.1073 $[M+H]^+$; found: 113.1078.

Mass-spectra (EI, 70 eV), m/z: 111 (33) $[M - H]^+$, 97 (4) $[M – CH_2 – H]^+$, 96 (3) $[M – CH_2 – 2 H]$,$^+$ 84 (63) $[M – (CH_2)_2]^+$, 83 (100) $[M – (CH_2)_2 - H]^+$, 56 (2) $[M – (CH_2)_4]^+$, 55 (10) $[M – (CH_2)_4 - H]^+$, 54 (21) $[M – (CH_2)_4 - 2H]^+$, 42 (14) $[M – (CH_2)_5]^+$, 41 (53) $[M – (CH_2)_4 - H]^+$, 32 (15) $[H_2N–NH_2]^+$, 30 (14) [M – ]$^+$, 29 (28) [M –  – H]$^+$, 27 (36) [M –  – 2H]$^+$.

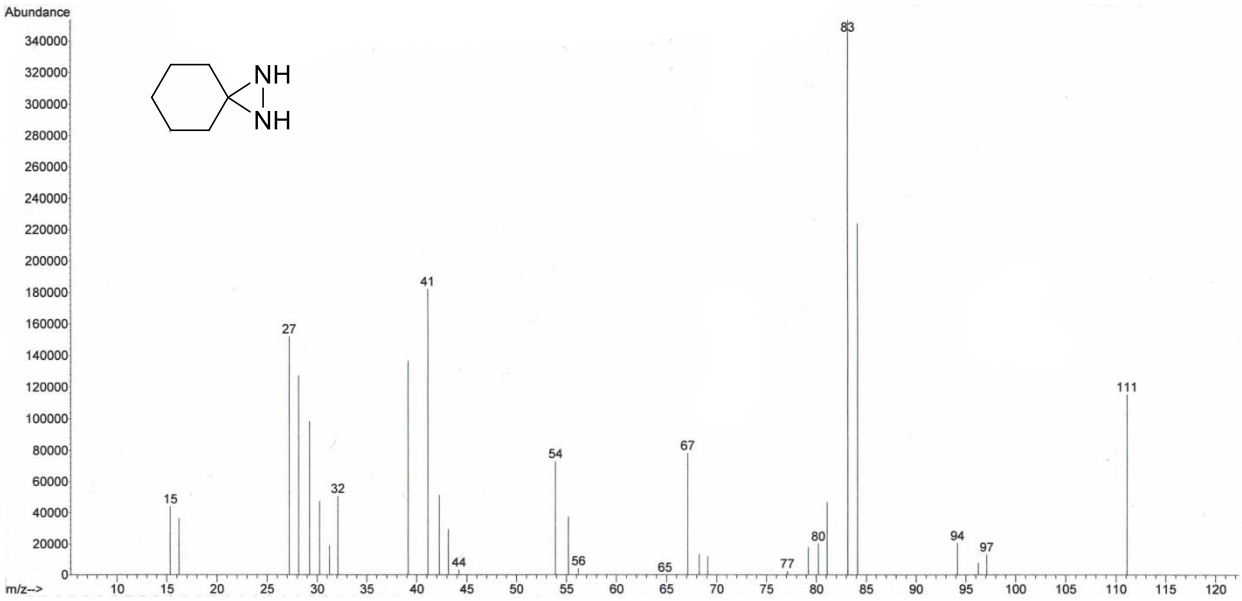

Figure S2. MS spectrum of PMDA.

References

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2. Gas-electron diffraction experiment

The electron diffraction patterns were recorded in the Moscow State University on the EG-100M apparatus using the R^3 sector made of brass. The electron wavelength was calibrated against gaseous CCl_4. The structural parameters of CCl_4 molecule were taken from Ref. S2. Information about the experimental conditions for all datasets used in the present investigation is given in Table S1.

Photo films (TASMA FT-41P) were scanned with the use of Epson Perfection Photo 4870 commercial scanner in the 16-bit/4800-dpi gray-scale scanning mode and VueScan computer program[S3]. This program enables one to retrieve data directly from the detector without any modifications. The data were processed using a computer program written by A.V.B. as in Ref. S4. Preliminarily, the high resolution was reduced by averaging over square regions of pixels as described in Ref. S4. With this method, mean transmittances and standard deviations were collected. The latter were used as weights for smoothing the transmittance surface with the use of 2D cubic splines[S5]. The calibration of the scanner was carried out against MD100 microdensitometer with the use of 24-bit gray-scale optical wedge of IT8 transmissive target on Kodak Ektachrome Professional E100G film[S6]. Displacements of the scanner were corrected against a special ruler manufactured by LOMO. After refinement of the center of electron diffraction pattern by the least squares method, the data of scanning were transformed into the total intensity curve taking into account 2D background. The atomic scattering factors were taken from Ref. S7.

References

[S2] S. Shibata, K. Iijima, R. Tani, and I. Nakamura, *Rep.Fac.Sci., Shizuoka Univ.* 1974, **9**, 33.

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[S7] A. W. Ross, M. Fink, and R. L. Hilderbrandt, in *International tables for crystallography, Vol. C*, Dodrecht: Kluwer Acad. Publ., 1992, 245.

Table S1 Experimental conditions of the gas-phase electron diffraction experiment for PMDA

	PMDA	
	LD	SD
Camera distance (mm)	362.3	193.9
Nozzle temperature (K)	331	333
Accelerating voltage (kV)	60	60
Vacuum (mm Hg)	$3.0 \cdot 10^{-5}$	$2.0 \cdot 10^{-5}$
Electron beam current (μA)	2.4	2.2
Electron wavelength (Å)	0.049992	0.050162
Number of films used	3	3
Range of s value ($Å^{-1}$)[a]	4.2–16.0	13.0–31.2

[a] $s = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle and λ is the electron wavelength. Experimental intensity curves were digitized with a step of 0.2 $Å^{-1}$.

3. Quantum chemical calculations and GED data

Table S2. Cartesian coordinates of PMDA (r_e, Å)

	CCSD(T) /VTZ			MP2/VQZ		
Atom	x	y	z	x	y	z
C1	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
C2	0.00000	0.00000	1.51186	0.00000	0.00000	1.50260
C3	1.44234	0.00000	2.03607	1.43628	0.00000	2.01918
C4	2.24360	1.16525	1.44411	2.22877	1.16064	1.42866
C5	2.23047	1.12167	-0.08836	2.21667	1.11015	-0.09496
C6	0.79101	1.12964	-0.61890	0.78430	1.12091	-0.62063
N7	-1.16918	-0.43251	-0.73591	-1.16079	-0.43934	-0.73503
N8	0.05871	-1.32313	-0.59995	0.06188	-1.31970	-0.59365
H9	-0.54290	-0.87997	1.86705	-0.54156	-0.87727	1.85693
H10	-0.52529	0.89401	1.86883	-0.52223	0.89150	1.85919
H11	1.91618	-0.94643	1.75334	1.90836	-0.94208	1.73354
H12	1.44494	0.04975	3.12793	1.44303	0.04618	3.10769
H13	3.27215	1.14092	1.81366	3.25357	1.14257	1.79848
H14	1.80543	2.11331	1.78004	1.78793	2.10477	1.75935
H15	2.78733	1.96663	-0.50107	2.77539	1.94728	-0.51183
H16	2.73553	0.20882	-0.42591	2.71603	0.19653	-0.42639
H17	0.30796	2.07832	-0.35726	0.30499	2.06759	-0.35976
H18	0.75725	1.03707	-1.70779	0.74508	1.02670	-1.70605
H19	-1.81984	-0.84804	-0.06915	-1.81187	-0.85602	-0.07294
H20	0.50020	-1.23122	-1.51497	0.50200	-1.23319	-1.50739

	MP2/VTZ			MP2(AE)/wcVTZ		
Atom	x	y	z	x	y	z
C1	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
C2	0.00000	0.00000	1.50458	0.00000	0.00000	1.50005
C3	1.43937	0.00000	2.01923	1.43466	0.00000	2.01418
C4	2.23040	1.16456	1.42840	2.22439	1.16055	1.42558
C5	2.21485	1.11897	-0.09771	2.20879	1.11576	-0.09596
C6	0.77893	1.12738	-0.62043	0.77735	1.12395	-0.61755
N7	-1.15951	-0.44740	-0.73824	-1.15603	-0.44542	-0.73566
N8	0.07301	-1.32296	-0.59251	0.07205	-1.31840	-0.59163
H9	-0.54008	-0.87926	1.85879	-0.53952	-0.87761	1.85362
H10	-0.52325	0.89120	1.86318	-0.52281	0.88941	1.85811
H11	1.91117	-0.94208	1.72958	1.90571	-0.94080	1.72611
H12	1.44919	0.04424	3.10873	1.44382	0.04387	3.10184
H13	3.25701	1.14694	1.79604	3.24918	1.14216	1.79273
H14	1.78877	2.10804	1.76315	1.78483	2.10280	1.76037
H15	2.77105	1.95988	-0.51279	2.76425	1.95513	-0.51027
H16	2.71606	0.20698	-0.43383	2.70978	0.20580	-0.43195
H17	0.29736	2.07300	-0.35597	0.29641	2.06803	-0.35409
H18	0.73767	1.03507	-1.70678	0.73628	1.03248	-1.70218
H19	-1.80475	-0.86889	-0.07114	-1.80307	-0.86525	-0.07220
H20	0.51350	-1.22762	-1.50686	0.51296	-1.22647	-1.50399

Table S2. (*continued*).

	MP2(FC)/wcVTZ			BTE		
Atom	x	y	z	x	y	z
C1	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
C2	0.00000	0.00000	1.50315	0.00000	0.00000	1.50678
C3	1.43785	0.00000	2.01796	1.43605	0.00000	2.03223
C4	2.22876	1.16318	1.42789	2.23758	1.15870	1.44207
C5	2.21330	1.11767	-0.09682	2.22777	1.11093	-0.08475
C6	0.77879	1.12609	-0.61938	0.79492	1.12103	-0.61723
N7	-1.15861	-0.44594	-0.73734	-1.16775	-0.42394	-0.73105
N8	0.07288	-1.32161	-0.59195	0.04681	-1.31653	-0.60074
H9	-0.54006	-0.87888	1.85716	-0.54385	-0.87670	1.86163
H10	-0.52319	0.89075	1.86169	-0.52388	0.89296	1.86127
H11	1.90954	-0.94189	1.72912	1.90948	-0.94533	1.75427
H12	1.44713	0.04427	3.10703	1.43547	0.05129	3.12165
H13	3.25492	1.14499	1.79546	3.26293	1.13372	1.81339
H14	1.78798	2.10653	1.76265	1.80142	2.10630	1.77398
H15	2.76944	1.95812	-0.51181	2.78647	1.95104	-0.49858
H16	2.71452	0.20614	-0.43281	2.73072	0.19800	-0.41761
H17	0.29752	2.07152	-0.35541	0.31447	2.06942	-0.35972
H18	0.73770	1.03393	-1.70539	0.76324	1.02724	-1.70380
H19	-1.80411	-0.86712	-0.07138	-1.82569	-0.83322	-0.07178
H20	0.51310	-1.22713	-1.50574	0.48849	-1.23602	-1.51372

	GED		
Atom	x	y	z
C1	0.00000	0.00000	0.00000
C2	1.50530	0.00000	0.00000
C3	2.03031	1.43465	0.00000
C4	1.44081	2.23536	1.15760
C5	-0.08451	2.22566	1.10982
C6	-0.61653	0.79427	1.11984
N7	-0.73021	-1.16665	-0.42347
N8	-0.60014	0.04672	-1.31519
H9	1.86987	-0.55887	-0.90079
H10	1.86854	-0.53669	0.91471
H11	1.74537	1.92021	-0.96939
H12	3.15008	1.43389	0.05275
H13	1.82257	3.28906	1.13191
H14	1.78063	1.78874	2.12802
H15	-0.50996	2.80006	1.97337
H16	-0.42545	2.74093	0.17445
H17	-0.35266	0.30201	2.09181
H18	-1.73292	0.76173	1.02350
H19	-0.05145	-1.84408	-0.84473
H20	-1.54005	0.50150	-1.23240

Table S3. Total $\Delta(r_{ij,e} - r_{ij,a})$ corrections to $r_{ij,a}$ internuclear distances; theoretical ($u_{ij,h1}$) and experimental ($u_{ij,exp}$) rms vibrational amplitudes (Å) for PMDA molecule

Type	*At.Num.*	$r_{ij,a}$	$r_{ij,e} - r_{ij,a}$[a]	$u_{ij,h1}$[b]	$u_{ij,exp}$
C C	1- 2	1.515	-0.0100	0.050	0.060(3)
C C	2- 3	1.538	-0.0100	0.052	0.061(3)
C C	3- 4	1.536	-0.0096	0.052	0.061(3)
C C	4- 5	1.536	-0.0096	0.052	0.061(3)
C C	5- 6	1.537	-0.0099	0.052	0.061(3)
C C	1- 6	1.515	-0.0100	0.050	0.060(3)
N C	1- 7	1.448	-0.0079	0.049	0.059(3)
N N	7- 8	1.524	-0.0123	0.056	0.065(3)
N C	1- 8	1.455	-0.0086	0.050	0.059(3)
C H	2- 9	1.137	-0.0162	0.077	0.086(3)
N H	7-19	1.064	-0.0161	0.072	0.081(3)
N C	2- 8	2.496	-0.0131	0.071	0.082(3)
N C	6- 7	2.508	-0.0103	0.071	0.081(3)
N C	6- 8	2.563	-0.0160	0.071	0.081(3)
N C	2- 7	2.570	-0.0127	0.070	0.081(3)
N C	3- 8	3.277	-0.0254	0.142	0.155(15)
N C	5- 8	3.327	-0.0265	0.140	0.154(15)
N C	5- 7	3.797	-0.0188	0.080	0.088(14)
N C	3- 7	3.838	-0.0209	0.079	0.087(14)
N C	4- 8	3.908	-0.0263	0.138	0.146(14)
N C	4- 7	4.352	-0.0179	0.077	0.116(47)
C C	1- 3	2.504	-0.0179	0.070	0.081(3)
C C	1- 5	2.506	-0.0172	0.070	0.080(3)
C C	4- 6	2.528	-0.0154	0.070	0.080(3)
C C	3- 5	2.530	-0.0140	0.069	0.080(3)
C C	2- 4	2.533	-0.0151	0.070	0.080(3)
C C	2- 6	2.541	-0.0139	0.067	0.078(3)
C C	1- 4	2.920	-0.0193	0.073	0.093(10)
C C	3- 6	2.960	-0.0151	0.074	0.094(10)
C C	2- 5	2.966	-0.0142	0.074	0.094(10)

[a] Calculated with the DFT- B2PLYP /VTZ cubic force constants (see text).
[b] Calculated with the DFT- B2PLYP /VTZ quadratic force constants (see text).

Table S4 . Correlation matrix for PMDA molecule

R(1,2)gr	100										
R(C-H)av	18	100									
u(1,2)gr	3	-42	100								
u(2,8)gr	14	-25	65	100							
u(3,8)gr	5	-15	12	5	100						
u(5,7)gr	2	-19	18	11	9	100					
u(4,7)gr	0	-3	0	2	-10	0	100				
u(7,20)gr	36	-4	22	31	2	3	0	100			
u(7,17)gr	-15	-5	7	-5	11	-9	1	-7	100		
scale1	9	-24	76	65	10	19	0	16	-2	100	
scale2	7	-27	76	59	12	16	2	19	11	61	100

Table S5. The Main equilibrium structural parameters of conformers of PMDA (bonds in Å, angles in deg.)

Parameters [a]	GED	BTE	CCSD(T)[b]	Parameters	GED	BTE	CCSD(T)[b]
C1-C2	1.505	1.507	1.512	H16–C5–C6	109.3	109.3	109.3
C3-C2	1.528	1.529	1.535	H17–C6–C1	108.5	108.5	108.6
C4-C3	1.526	1.528	1.533	H18–C6–C1	109.2	109.2	109.2
C5-C4	1.526	1.528	1.533	H19–N7–C1	108.3	108.3	107.7
C6-C5	1.527	1.529	1.534	H20–N8–C1	108.3	108.3	107.8
C1-C6	1.505	1.507	1.512	C4–C3–C2–C1	54.4	54.4	54.5
N7-C1	1.440	1.442	1.448	C5–C4–C3–C2	-56.6	-56.6	-56.6
N8-N7	1.511	1.513	1.523	C6–C5–C4–C3	56.7	56.7	56.6
C1-N8 [b]	1.446	1.448	1.454	C1–C6–C5–C4	-54.8	-54.8	-54.8
(C-H)av	1.121	1.091	1.093	C2–C1–C6–C5 [b]	55.0	55.0	55.3
(N-H)av	1.047	1.017	1.020	C3–C2–C1–C6 [b]	-54.7	-54.7	-55.0
C3–C2–C1	110.1	110.1	110.0	N7–C1–C2–C3	160.1	160.0	159.7
C4–C3–C2	111.1	111.1	111.1	N8–N7–C1–C2	-104.0	-104.0	-103.9
C5–C4–C3	111.0	111.0	111.1	H9–C2–C3–C4	175.1	175.1	175.1
C6–C5–C4 [b]	110.7	110.7	110.7	H10–C2–C3–C4	-65.5	-65.5	-65.4
C1–6C–C5 [b]	110.3	110.3	110.2	H11–C3–C4–C5	63.2	63.2	63.1
C2–C1–C6 [b]	114.2	114.2	114.2	H12–C3–C4–C5	-179.1	-179.1	-179.1
N7–C1–C2	120.5	120.5	120.6	H13–C4–C5–C6	179.0	179.0	179.0
H9–C2–C3	110.9	110.9	110.8	H14–C4–C5–C6	-63.8	-63.8	-63.9
H10–C2–C3	109.8	109.8	109.8	H15–C5–C6–C1	-177.4	-177.4	-177.4
H11–C3–C4	109.3	109.3	109.3	H16–C5–C6–C1	65.4	65.4	65.4
H12–C3–C4	110.5	110.5	110.5	H17–C6–C1–C2	-65.0	-65.0	-64.7
H13–C4–C5	110.2	110.2	110.2	H18–C6–C1–C2	178.4	178.4	178.6
H14–C4–C5	109.1	109.1	109.1	H19–N7–C1–C2	-9.5	-9.5	-9.7
H15–C5–C6	110.1	110.1	110.1	H20–N8–C1–C2	-152.6	-152.6	-152.7

[a] *R*-factor = 5.0 %. For the two groups of refined internuclear distances (C/N–H and all residual internuclear distances, in Å) 3σ standard deviations of the LS refinement were 0.006 Å. Valence angles were set equal to the best theoretical BTE values. The numbering of atoms is shown in Figure S1.
[b] CCSD(T)/cc-pVTZ level of theory.
[c] Ring closure parameters (in degrees).

4. NMR spectroscopy data

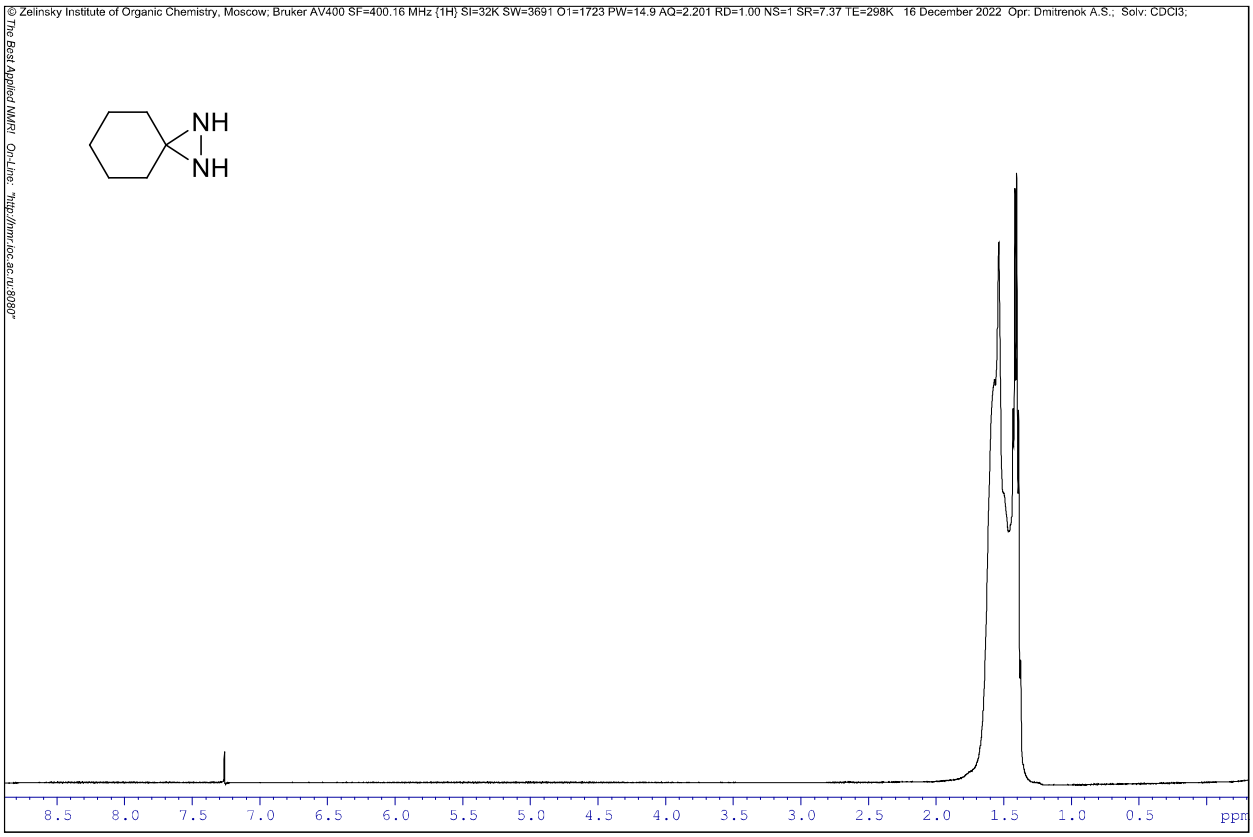

Figure S3. ^{1}H NMR spectrum of PMDA ($CDCl_3$, 298 K).

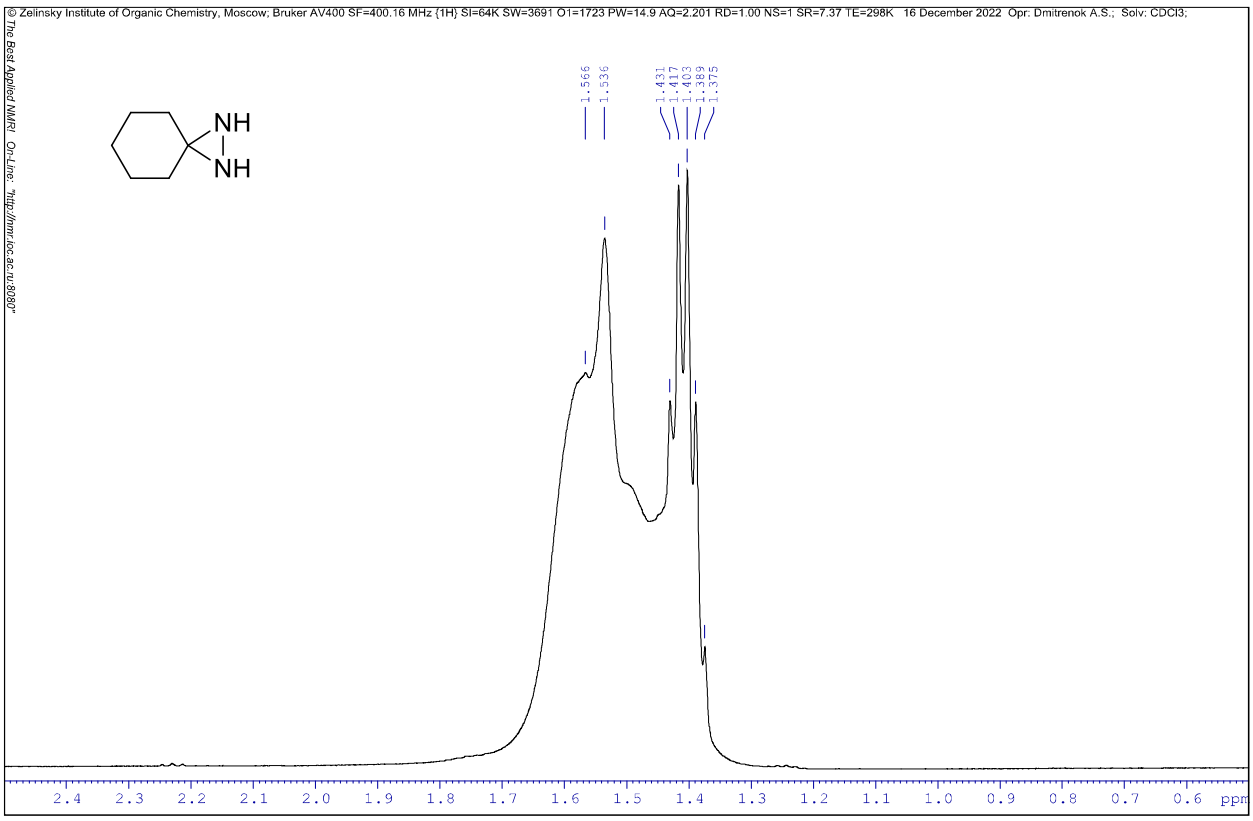

Figure S4. Fragment of the ^{1}H NMR spectrum of PMDA, ($CDCl_3$, 298 K).

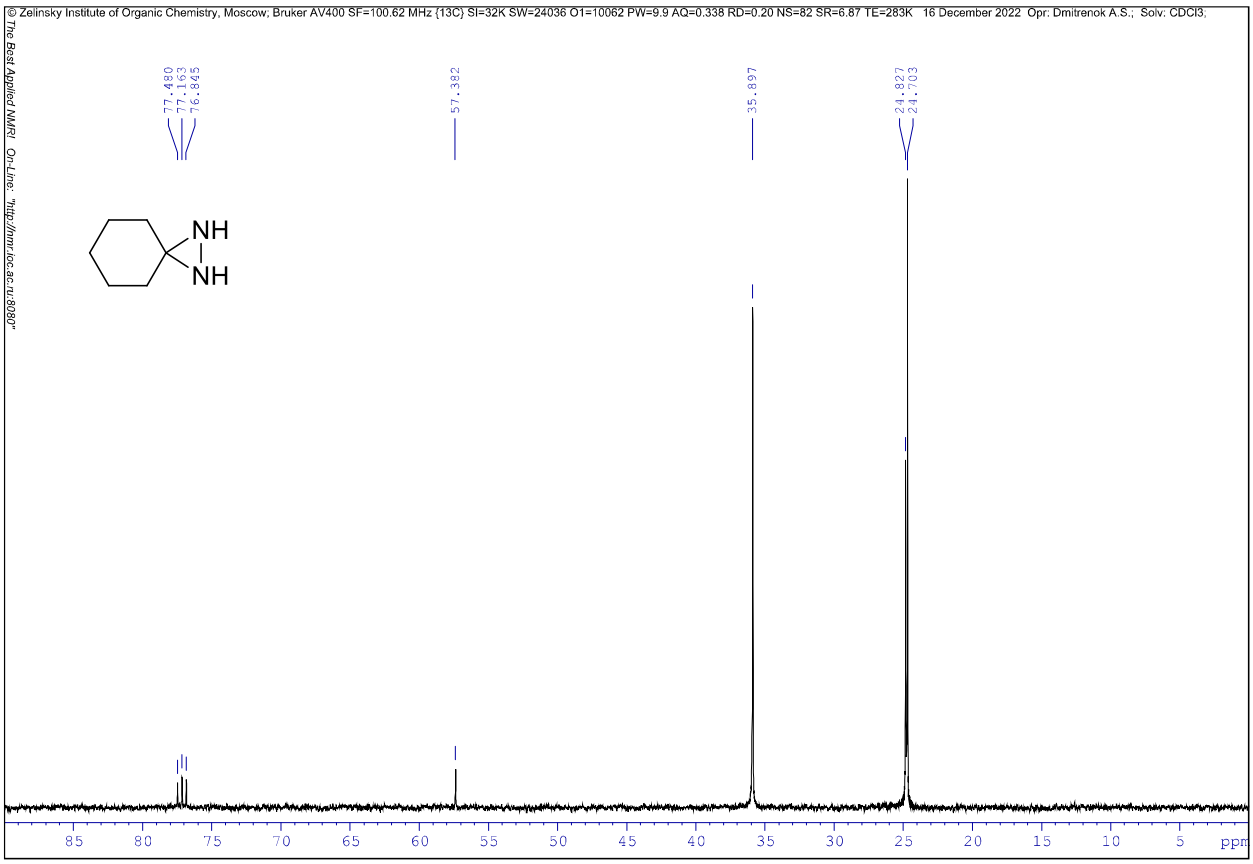

Figure S5. ^{13}C NMR spectrum of PMDA ($CDCl_3$, 283 K).

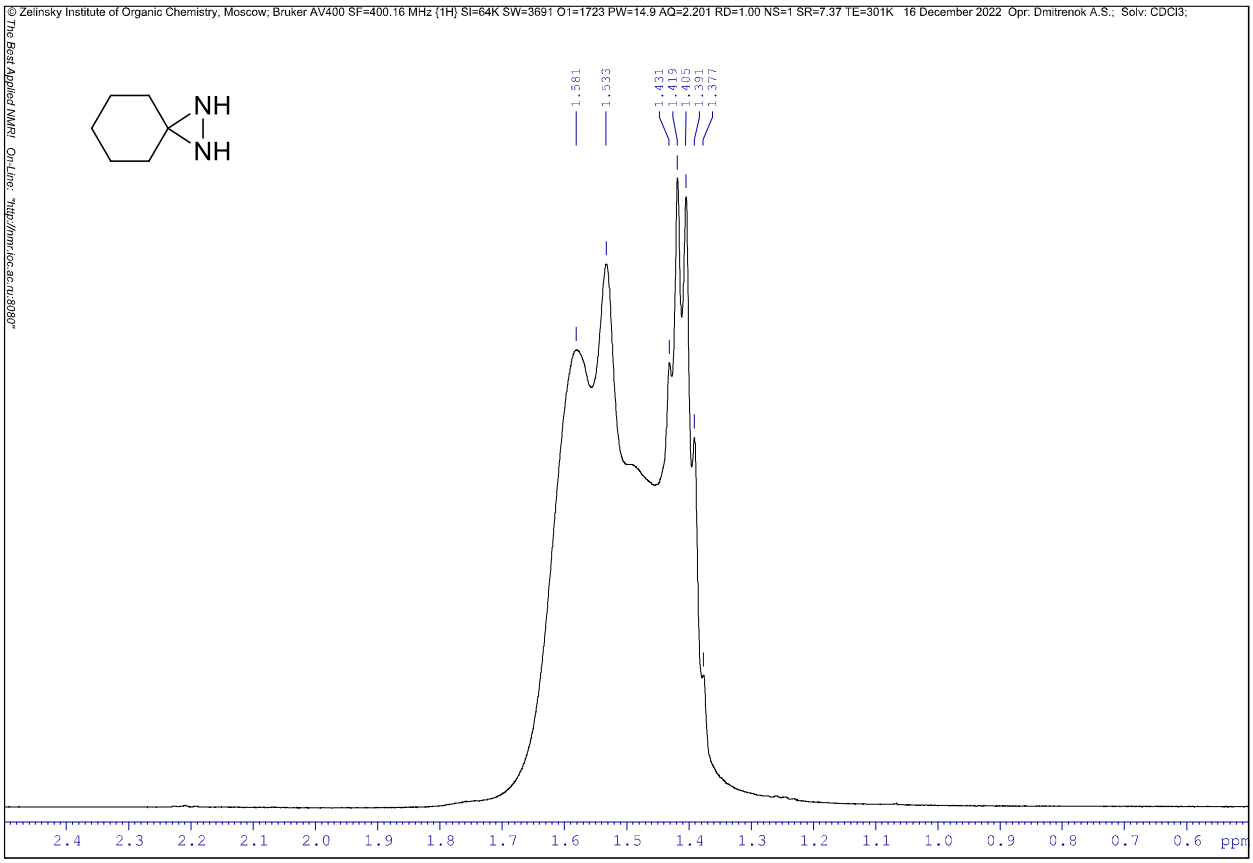

Figure S6. Fragment of the ^{1}H NMR spectrum of PMDA ($CDCl_3$, 302 K).

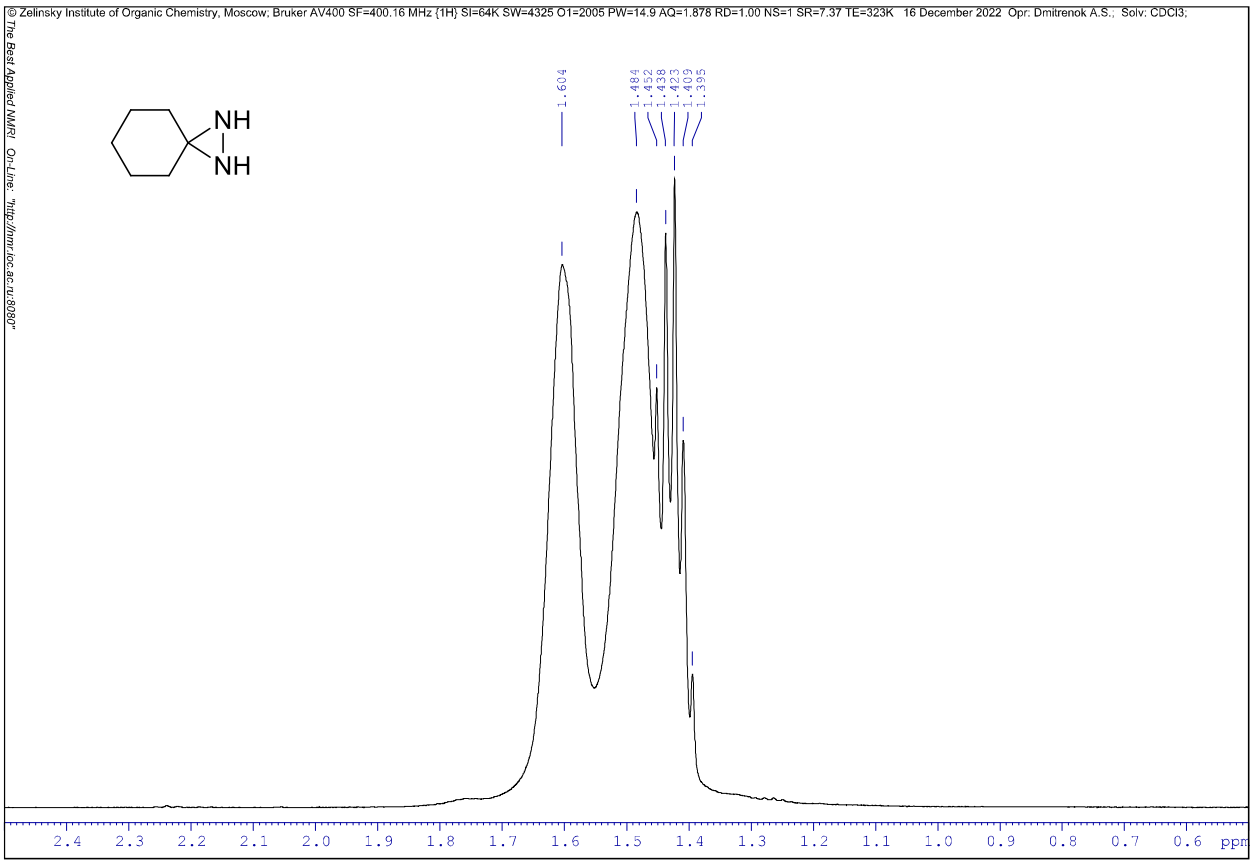

Figure S7. Fragment of the ^{1}H NMR spectrum of PMDA ($CDCl_3$, 323 K)

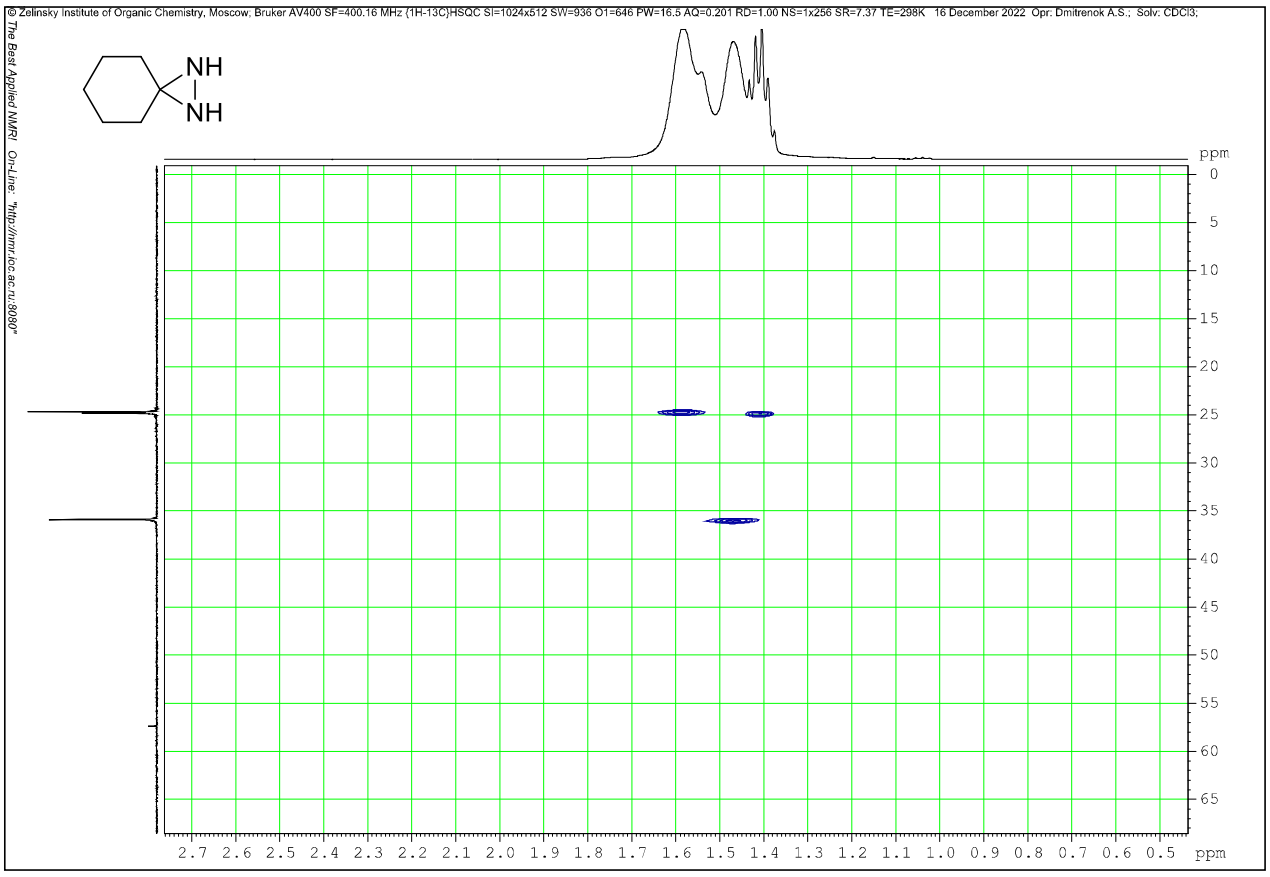

Figure S8. {^{1}H-^{13}C}HSQC spectrum of PMDA ($CDCl_3$, 298 K).

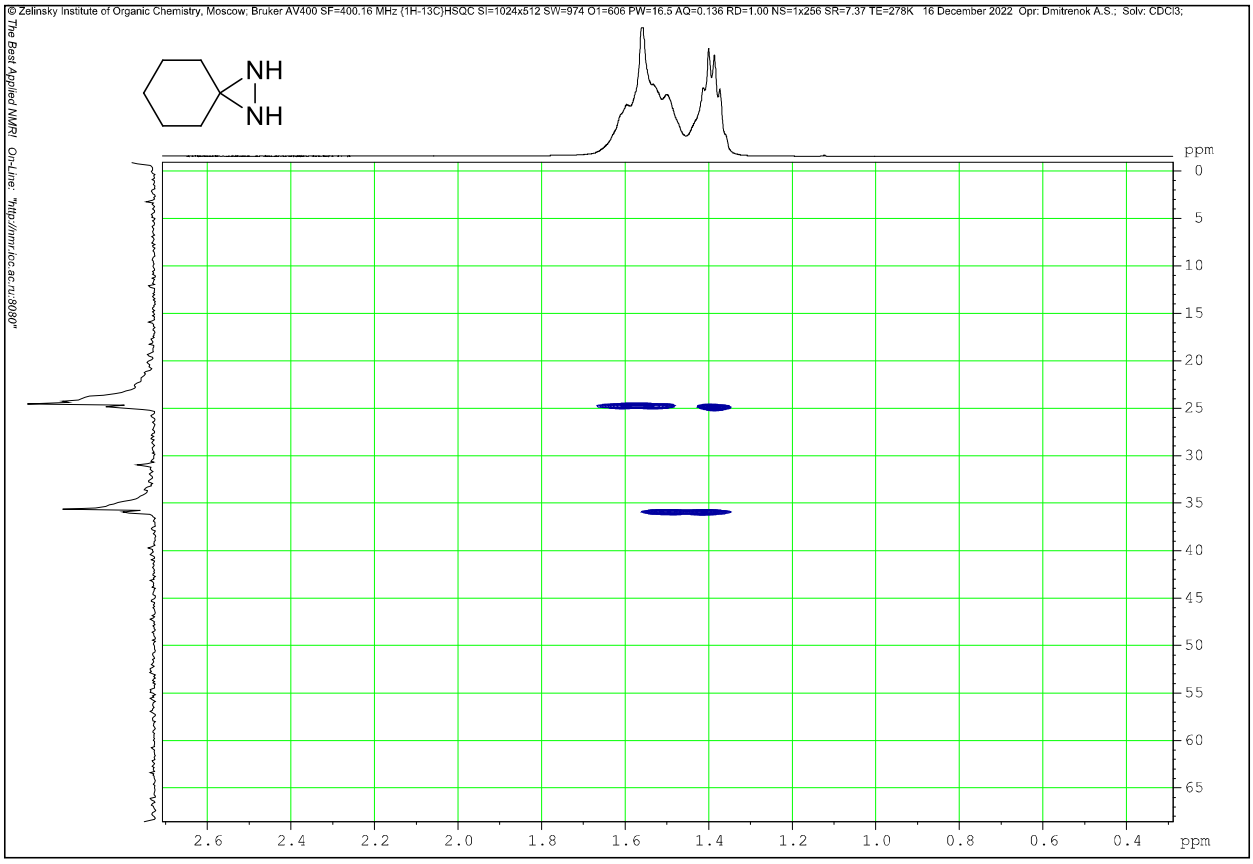

Figure S9. {^{1}H-^{13}C}HSQC spectrum of PMDA ($CDCl_3$ 273 K).

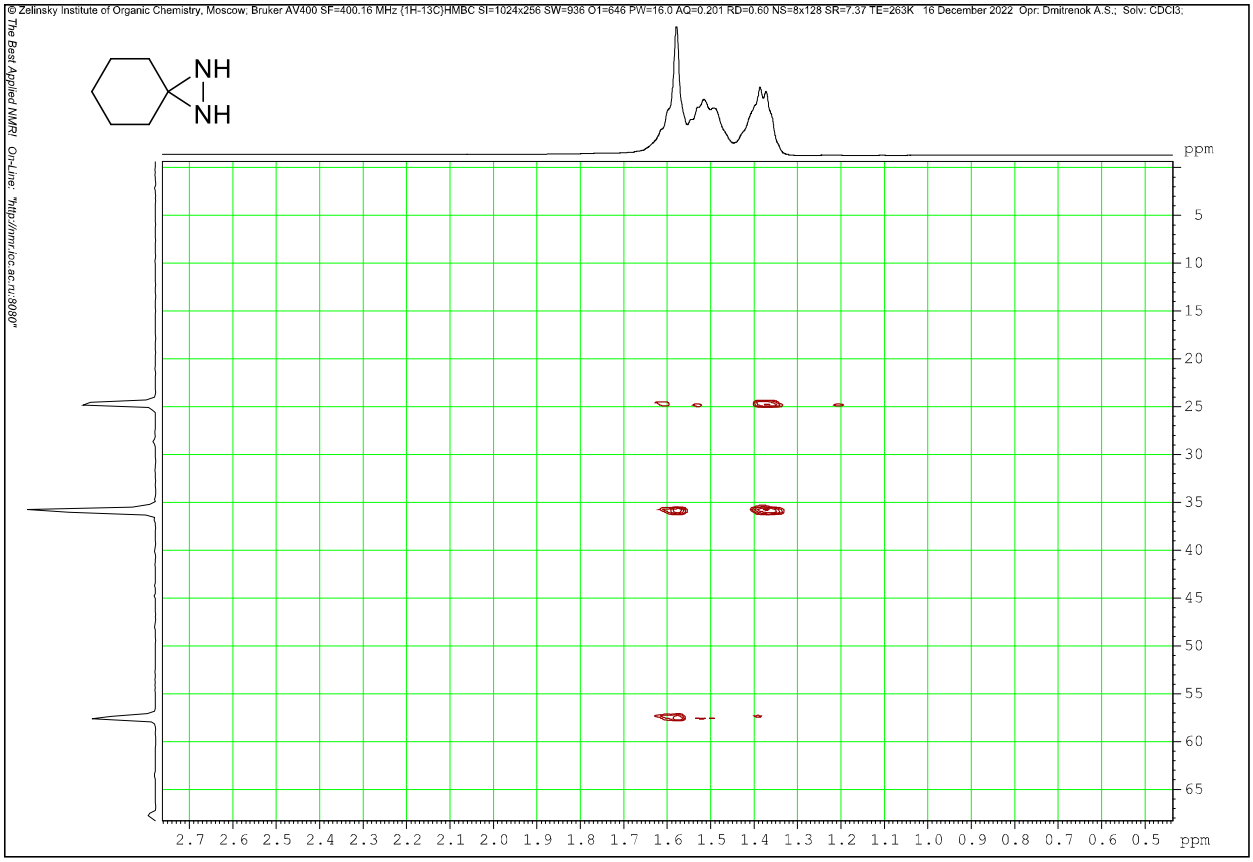

Figure S10. {^{1}H-^{13}C}HMBC spectrum of PMDA ($CDCl_3$, 263 K).

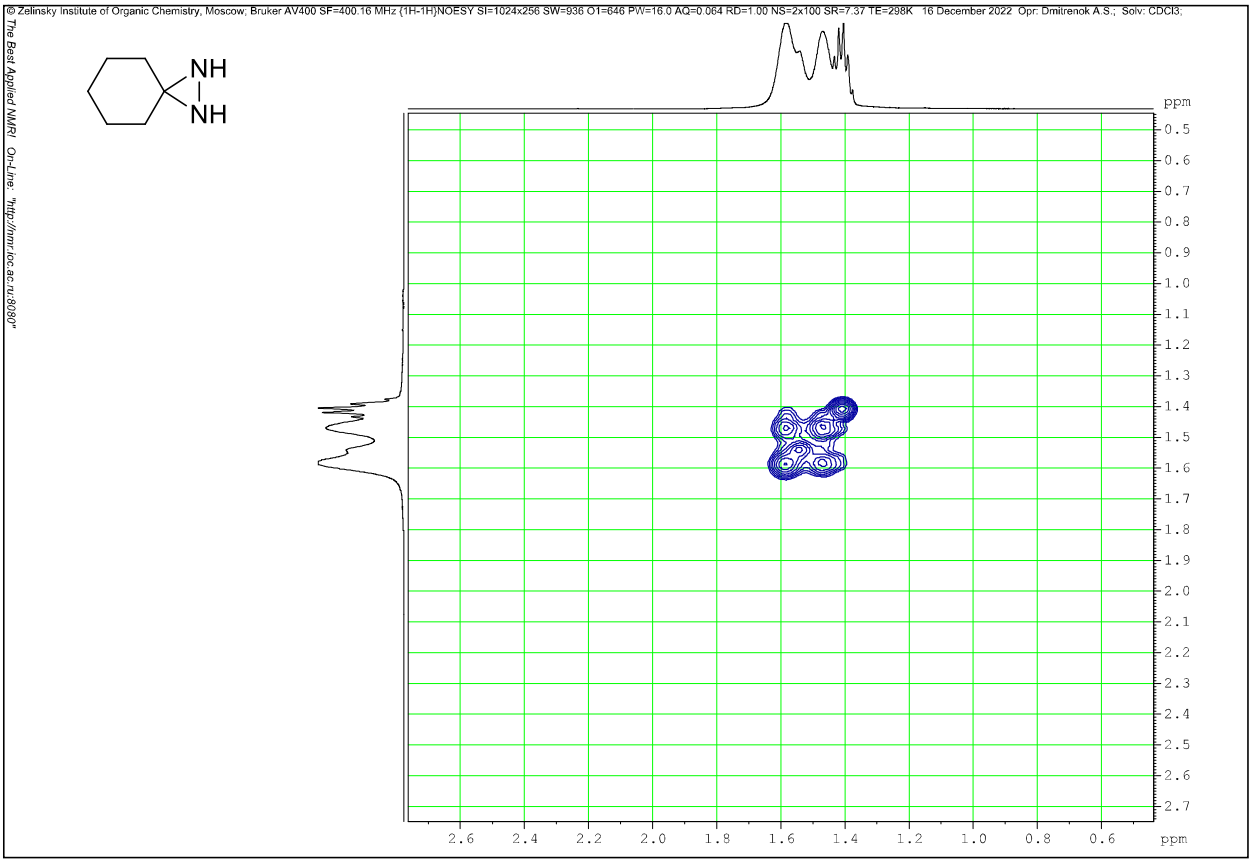

Figure S11. {^{1}H–^{1}H}gNOESY spectrum of PMDA ($CDCl_3$, 298 K).

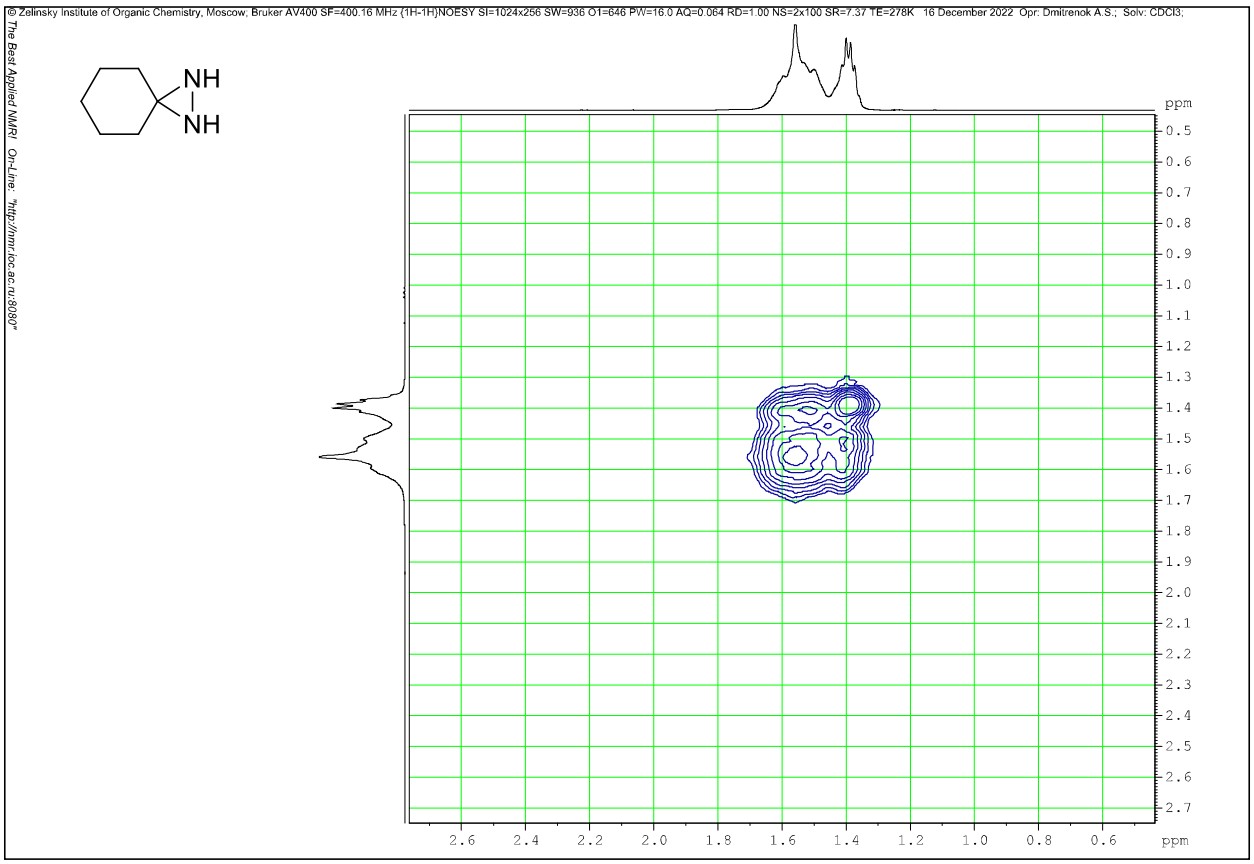

Figure S12. {^{1}H–^{1}H}gNOESY spectrum of PMDA ($CDCl_3$, 278 K).

Table S6. The {^{1}H-^{13}C}HSQC, and {^{1}H-^{13}C}HMBC data for PMDA (Figs. S8, S10). Atom numbering is shown in Fig. S1.

Atom numbers	^{13}C NMR chemical shift, ppm	{^{1}H-^{13}C}HSQC interactions	{^{1}H-^{13}C}HMBC interactions
C1	57.4	-	H9, H10, H17, H18, H19, H20
C2	35.9	H9, H10	H11, H12, H13, H14, H19, H20
C3	24.7	H11, H12	H9, H10, H13, H14, H15, H16
C4	24.4	H14, H13	H9, H10, H11, H12, H15, H16, H17, H18
C5	24.7	H15, H16	H11, H12, H13, H14, H17, H18
C6	35.9	H17, H18	H13, H14, H15, H16, H19, H20

In the {^{1}H- ^{1}H}gNOESY spectrum of PMDA proton H13 has cross-peaks with protons H11, H16. Proton H14 has cross-peaks with protons H12, H15. (Fig. S11).