Do primary nitrosamines form and exist in the gas phase? A computational study of

CH_3NHNO and $(CH_3)_2NNO$.

Electronic Supplementary Information

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Figure S1. The optimized geometries at the B3LYP/6-311++G(d,p), B3LYP/aug-cc-pVDZ, MP2/6-311++G(d,p), and MP2/aug-cc-pVDZ levels for the $(CH_3)_2N$ +NO reaction. Bond distances are in angstrom and bond angles are in degrees. For SP3, the values are from the B3LYP/6-311++G(d,p) and B3LYP/aug-cc-pVDZ levels.

Figure S2. The optimized geometries at the B3LYP/6-311++G(d,p), B3LYP/aug-cc-pVDZ, MP2/6-311++G(d,p), and MP2/aug-cc-pVDZ levels for the CH₃NH+NO reaction. Bond distances are in angstrom and bond angles are in degrees. For SP8 the values are from the B3LYP/6-311++G(d,p) and B3LYP/aug-cc-pVDZ levels.
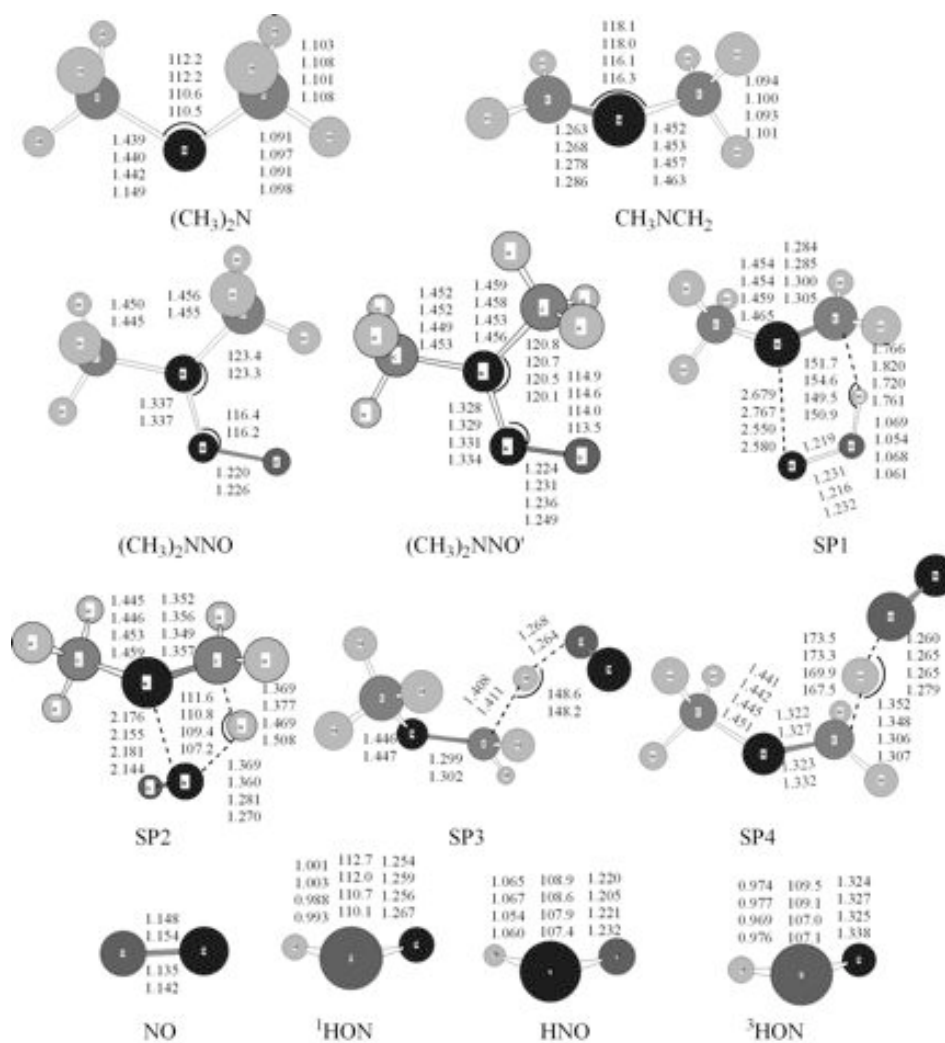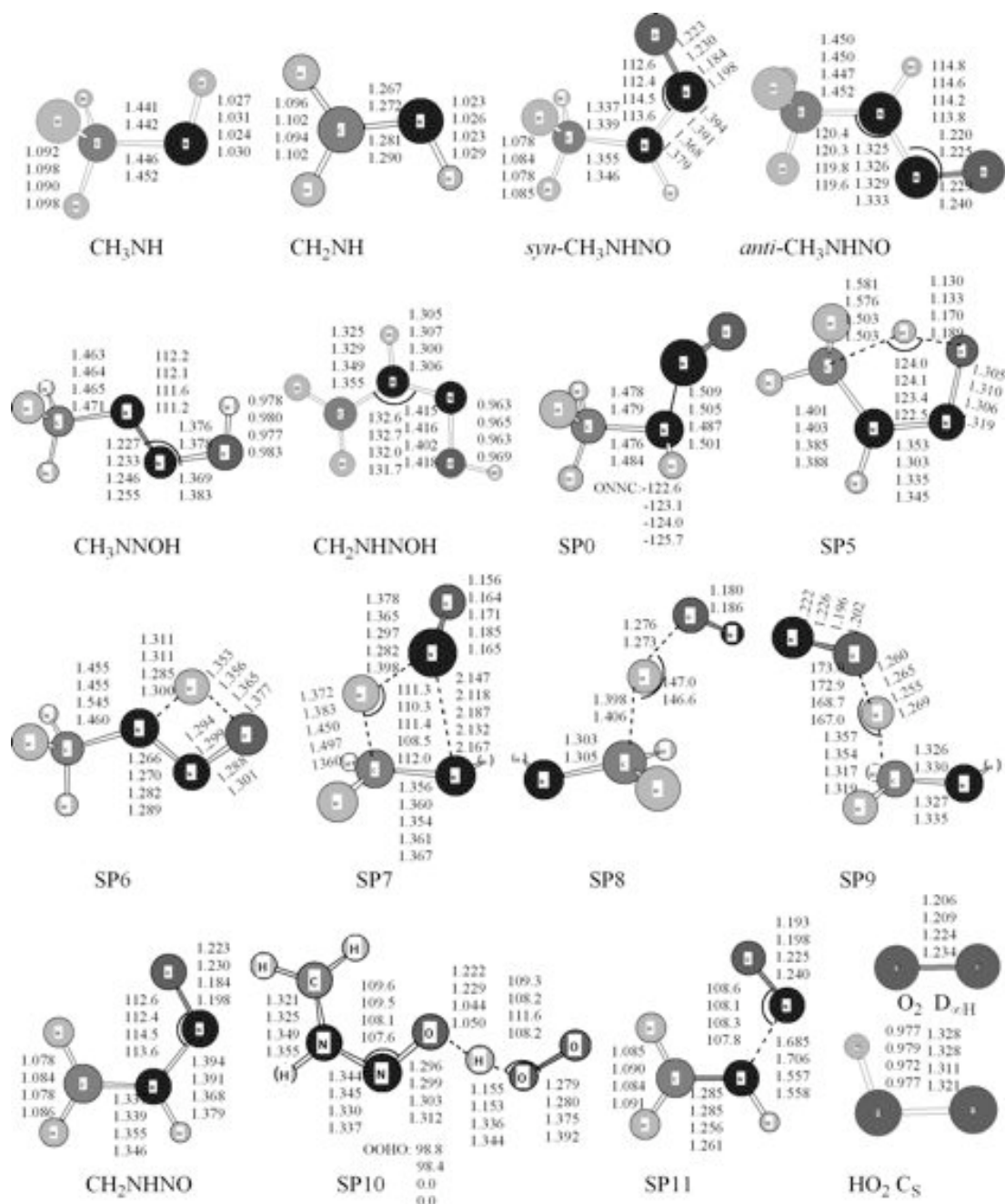
Table S1. The relative energies (ΔE_{elec}, including ZPE) and enthalpies (ΔH_{298}) at 298 K (kJ mol^{-1}) for the $(CH_3)_2N + NO$ reaction system at the various levels.

Species	B3LYP/6-311++G(d,p)		B3LYP/aug-cc-pVDZ		MP2/6-311++G(d,p)		MP2/aug-cc-pVDZ		G4	
	ΔE_{elec}	ΔH_{298}	ΔE_{elec}	ΔH_{298}	ΔE_{elec}	ΔH_{298}	ΔE_{elec}	ΔH_{298}	ΔE_{elec}	ΔH_{298}
$(CH_3)_2N+NO$	0	0	0	0	0	0	0	0	0	0
$HNO+CH_3NCH_2$	-41.6	-42.9	-41.4	-42.8	-81.7	-83.1	-86.2	-87.5	-61.4	-61.4
$^1HON+CH_3NCH_2$	126.5	125.2	125.4	124.0	121.7	120.4	116.9	115.6	116.1	116.1
$^3HON+CH_3NCH_2$	42.7	41.4	40.7	39.3	31.6	30.4	26.0	24.7	47.7	47.7
$(CH_3)_2NNO$	-169.2	-174.2	-172.3	-177.3					-185.3	-185.8
$(CH_3)_2NNO´$	-169.0	-174.1	-172.4	-177.8	-210.0	-215.1	-220.0	-225.5	-187.1	-187.1
SP1	123.0	117.8	120.7	115.8	120.9	115.3	108.2	102.7	109.2	106.7
SP2	68.3	62.4	62.6	56.6	19.2	13.4	-1.2	-7.9	52.7	50.2
SP3	140.0	135.8	135.4	131.1	165.0	162.0	128.5	123.5	141.3	138.9
SP4	111.1	108.2	106.8	103.8	214.4	211.4	204.1	201.1	155.0	152.5

Table S2. The relative energies (ΔE_{elec}, including ZPE) and enthalpies (ΔH_{298}) at 298 K (kJ mol^{-1}) for the $CH_3NH + NO$ reaction system at the various levels.

Species	B3LYP/6-311++G(d,p)		B3LYP/aug-cc-pVDZ		MP2/6-311++G(d,p)		MP2/aug-cc-pVDZ		G4	
	ΔE_{elec}	ΔH_{298}	ΔE_{elec}	ΔH_{298}	ΔE_{elec}	ΔH_{298}	ΔE_{elec}	ΔH_{298}	ΔE_{elec}	ΔH_{298}
CH_3NH+NO	0	0	0	0	0	0	0	0	0	0
$CH_2NH+HNO$	-52.7	-52.9	-52.9	-53.1	-89.8	-89.8	-95.0	-95.1	-73.3	-73.3
CH_2NH+^1HON	115.3	115.2	113.8	113.7	113.7	223.7	108.1	108.0	104.3	104.3
CH_2NH+^3HON	31.5	31.4	29.1	29.0	23.6	23.6	17.2	17.2	35.9	35.9
syn-CH_3NHNO	-181.9	-187.0	-185.6	-190.8	-213.0	-217.5	-221.5	-226.8	-195.6	-198.1
$anti$-CH_3NHNO	-179.1	-184.2	-182.6	-187.7	-207.4	-212.0	-214.1	-219.0	-190.1	-192.6
CH_3NNOH	-176.3	-181.9	-182.5	-188.2	-214.5	-220.0	-223.2	-228.8	-200.1	-202.6
CH_2NHNOH	-60.5	-66.5	-66.6	-72.7	-96.5	-103.8	-107.5	-113.1	-79.0	-81.5
SP0	-84.8	-91.6	-89.2	-96.0	-125.6	-132.5	-133.9	-140.7	-114.0	-116.5
SP5	-5.4	-25.6	-16.4	-24.6	-52.3	-60.5	-69.8	-77.9	-25.0	-27.4
SP6	-49.8	-55.5	-58.9	-64.7	-88.7	-94.2	-103.3	-108.9	-69.0	-71.5
SP7	58.6	53.0	52.6	47.0	19.6	14.4	0.6	-4.8	47.8	45.3
SP8	113.8	129.5	128.6	124.3	141.6	136.9	126.2	121.5	134.1	131.6
SP9	111.6	108.9	107.0	104.2	216.2	213.4	206.0	203.1	155.8	153.3

Table S3. The relative energies (ΔE_{elec}, including ZPE) and enthalpies (ΔH_{298}) at 298 K (kJ mol^{-1}) for the $CH_3NH + NO+O_2$ reaction system at the various levels.

Species	B3LYP/6-311++G(d,p)		B3LYP/aug-cc-pVDZ		MP2/6-311++G(d,p)		MP2/aug-cc-pVDZ		G4	
	ΔE_{elec}	ΔH_{298}	ΔE_{elec}	ΔH_{298}	ΔE_{elec}	ΔH_{298}	ΔE_{elec}	ΔH_{298}	ΔE_{elec}	ΔH_{298}
$CH_3NH+NO+O_2$	0	0	0	0	0	0	0	0	0	0
$CH_2NHNO+HO_2$	-19.3	-24.5	-25.5	-30.8	45.9	41.4	33.9	28.7	-18.4	-23.4
$CH_2NH+NO+HO_2$	-60.0	-60.1	-58.9	-59.0	-44.8	-44.9	-46.7	-46.8	-77.7	-80.2
syn-$CH_3NHNO+O_2$	-181.9	-187.0	-185.6	-190.8	-213.0	-217.5	-221.5	-226.8	-195.6	-198.1
$CH_2NHNOH+O_2$	-65.0	-66.5	-66.6	-72.7	-96.5	-103.8	-107.5	-113.1	-79.0	-81.5
$SP5+O_2$	-5.4	-25.6	-16.4	-24.6	-52.3	-60.5	-69.8	-77.9	-25.0	-27.4
SP10	88.4	80.6	82.4	74.6	90.8	82.9	77.3	68.1	31.0	26.0
$SP11+HO_2$	-8.5	-13.3	-11.2	-16.0	83.0	77.5	66.4	60.6	-0.2	-5.2

Table S4. The vertical excitation energy T_V (eV) and oscillator strength f (atomic units) of the $(CH_3)_2NNO$ at the various DFT methods with the aug-cc-pVTZ geometry.

State	Exp.[a]	B3LYP		BP86		X3LYP		PW1PW91		PBE1PBE	
	T_V	T_V	f	T_V	f	T_V	f	T_V	f	T_V	f
1A″	3.41	3.46	0.0010	3.43	0.0011	3.46	0.0010	3.52	0.0011	3.52	0.0011
2A′	5.46	5.91	0.1413	5.52	0.1273	5.94	0.1173	6.08	0.1900	6.08	0.1913

[a] G. Geiger, H. Stafast, U. Bruehlmann and J. R. Huber, *Chemical Physics Letters*, 1981, **79**, 521-524.

Table S5. The vertical excitation energy (in eV) of $(CH_3)_2NNO$ at the B3LYP/basis set//B3LYP/6-311++G(d,p) geometry.

State	Exp.[a]	6-311++G(d,p)	cc-pVDZ	cc-pVTZ	cc-pVQZ	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ
1A″	3.41	3.44	3.46	3.46	3.45	3.45	3.45	3.44
2A´	5.46	5.91	6.14	5.99	5.98	5.88	5.87	5.87

[a] G. Geiger, H. Stafast, U. Bruehlmann and J. R. Huber, *Chemical Physics Letters*, 1981, **79**, 521-524.

Table S6. The vertical excitation energy (eV) of the $(CH_3)_2NNO$ at the various basis sets with the B3LYP/basis set//B3LYP/basis set.

State	Exp.[a]	6-311++G(d,p)	cc-pVDZ	cc-pVTZ	cc-pVQZ	aug-cc-pVDZ	aug-cc-pVTZ
1A″	3.41	3.44	3.45	3.47	3.47	3.43	3.46
2A´	5.46	5.91	6.05	6.01	6.02	5.85	5.91

[a] G. Geiger, H. Stafast, U. Bruehlmann and J. R. Huber, *Chemical Physics Letters*, 1981, **79**, 521-524.

Table S7. The vertical excitation energy (in eV) of the $(CH_3)_2NNO$ at the CASPT2 and MR-CI methods with different basis set.

State	Exp.[a]	cc-pVDZ		cc-pVTZ		aug-cc-pVDZ		aug-cc-pVTZ
		CASPT2	MRCI	CASPT2	MRCI	CASPT2	MRCI	CASPT2
1A″	3.41	4.03	4.09	3.45	3.47	3.54	3.36	3.43
2A´	5.46	6.25	6.27	5.55	6.02	5.45	5.84	5.46

[a] G. Geiger, H. Stafast, U. Bruehlmann and J. R. Huber, *Chemical Physics Letters*, 1981, **79**, 521-524.

Table S8. The vertical excitation energy T_V (eV) and oscillator strength f (atomic units) of the first excited state (1A") of the CH_3NHNO, CH_3NNOH CH_2NHNOH and CH_3NHNO_2 at various DFT methods with the aug-cc-pVTZ geometry.

Species	State	B3LYP		BP86		X3LYP		PW1PW91		PBE1PBE	
		T_V	f	T_V	f	T_V	f	T_V	f	T_V	f
CH_3NHNO	1A"	3.43	0.0012	3.38	0.0011	3.44	0.0012	3.49	0.0013	3.49	0.0012
	2A´	5.23	0.0056	4.61	0.0068	5.25	0.0058	5.46	0.0056	5.49	0.0058
CH_3NNOH	1A"	4.70	0.0000	4.63	0.0000	4.71	0.0000	4.77	0.0000	4.78	0.0000
	2A´	6.47	0.0673	5.97	0.0604	6.51	0.0650	6.69	0.0805	6.69	0.0902
CH_2NHNOH	1A"	3.81	0.0047	3.77	0.0048	3.77	0.0048	3.92	0.0053	3.97	0.0053
	2A"	4.35	0.0018	4.25	0.0009	4.32	0.0019	4.47	0.0018	4.53	0.0022

Table S9. The PCM-TDDFT vertical excitation energy (eV) and oscillator strength (atomic units) of $(CH_3)_2NNO$, CH_3NHNO, CH_3NNOH, and CH_2NHNOH in various solvents at the B3LYP/aug-cc-pVTZ level.

Species	n-hexane		ethanol		methanol		nitromethane		water		gas phase	
	T_V	f	T_V	f	T_V	f	T_V	f	T_V	f	T_V	f
$(CH_3)_2NNO$	3.50	0.0015	3.59	0.0015	3.5	0.0015	3.59	0.0015	3.60	0.0015	3.49	0.0010
	3.53[a]		3.58[a]						3.70[b]		3.41[c]	
CH_3NHNO	3.45	0.0014	3.56	0.0018	3.56	0.0014	3.56	0.0015			3.43	0.0012
CH_3NNOH	4.68	0.0000	4.67	0.0000	4.67	0.0000	4.67	0.0000			4.70	0.0000
CH_2NHNOH	3.95	0.0067	4.10	0.0117	4.11	0.0118	4.11	0.0120			3.81	0.0047

[a] From R. N. Haszeldine and J. Jander, *Journal of the Chemical Society*, **1954**, 691-695. [b] From M. H. Plumlee and M. Reinhard, *Environmental Science & Technology* **2007**, *41* (17), 6170-6176. [c] G. Geiger, H. Stafast, U. Bruehlmann and J. R. Huber, *Chemical Physics Letters*, 1981, **79**, 521-524.