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Direct Observation of Methoxycarbonylnitrene

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Experimental details

Synthesis of $CH_3OC(O)N_3$ and $CH_3OC(O)NCO$.

Caution! Covalent azides are potentially hazardous and explosive. Although we have not experienced any incident during this work, safety precautions (face shields and leather gloves) are recommended for handling the azide in the condensed phases.

Methyl azidoformate ($CH_3OC(O)N_3$) was prepared according to previous literature.[1] Its purity was checked by gas phase IR spectroscopy and ^1H and ^{13}C NMR spectroscopy ($CDCl_3$, 400 MHz). For the preparation of ^{15}N-labelled $CH_3OC(O)N_3$, 1-^{15}N sodium azide (98 atom % ^{15}N, EURISO-TOP GmbH) was used. The methyl azidoformate-d_3 was prepared according to published protocol.[2] Methoxycarbonyl isocyanate ($CH_3OC(O)NCO$) was prepared according to the reference[3] with modification. Briefly, it was prepared by the slow addition of oxalyl chloride (0.1 mol) to a solution of methyl carbamate (0.1 mol) in dichloromethane (10 mL). The mixture was stirred for 30 min at room temperature. The solvent and byproducts (dichloromethane and mainly hydrogen chloride) were removed by distillation. Then the residue was purified by repeated trap-to-trap condensation (–45 °C, –90 °C, –196 °C) in vacuum. The product $CH_3OC(O)NCO$ was collected in the –45 °C trap as a colorless liquid. The purity of $CH_3OC(O)NCO$ was checked by gas phase IR spectroscopy and ^1H and ^{13}C NMR spectroscopy ($CDCl_3$, 400 MHz).

Matrix-isolation IR spectroscopy.

Matrix IR spectra were recorded on a FT-IR spectrometer (Bruker 70V) in a reflectance mode by using a transfer optic. A KBr beam splitter and MCT detector were used in the mid-IR region (4000–600 cm^{-1}). For each spectrum, 200 scans at a resolution of 0.5 cm^{-1} were co-added.

The gaseous sample was mixed with inert gas (Ne, Ar, N_2) with a ratio of 1:1000 (estimated) in a 1 L stainless-steel container. Then a small amount (ca. 1 mmol) of the mixture was deposited (2 mmol/h) onto the cold matrix support (2.8 K, gold-plated copper block) in a high-level vacuum (~10^{-6} Pa) within 30 minutes. Photolysis experiments were carried out with an ArF excimer laser (Gamlaser EX5/250, 193 nm, 3Hz), Nd^{3+}:YAG laser (266 nm, MPL-F-266, 10 mW) and an ultraviolet lamp (40W, 365 nm).

Matrix-isolation EPR spectroscopy.

EPR spectra were recorded using a Bruker ELEXSYS E500 spectrometer operating at the X-band equipped with a digital temperature controller. For the measurements under the organic glassy matrix conditions, the sample solution (20 mg mL^{-1}) in a quartz tube (4.0 mm) was degassed by the freeze-pump-thaw cycle for three times. After the sample deposition, the cryostat cold head was cooled to 5 K for photolysis and measurement.

Quantum chemical calculation methods.

Structures and IR frequencies of stationary points were calculated using the DFT methods (B3LYP,[4] BP86,[5] M06-2X.[6]) with the 6-311++G(3df,3pd) basis set. Accurate relative energies of the species were further calculated using the complete basis set (CBS-QB3).[7] Time-dependent (TD) DFT (B3LYP/6-311++G(3df,3pd)) calculations[8] were performed for the prediction of UV-vis transitions. Local minima were confirmed by vibrational frequency analysis, and transition states were further confirmed by intrinsic reaction coordinate (IRC) calculations.[9] All the calculations were performed using the Gaussian 09 software package.[10]

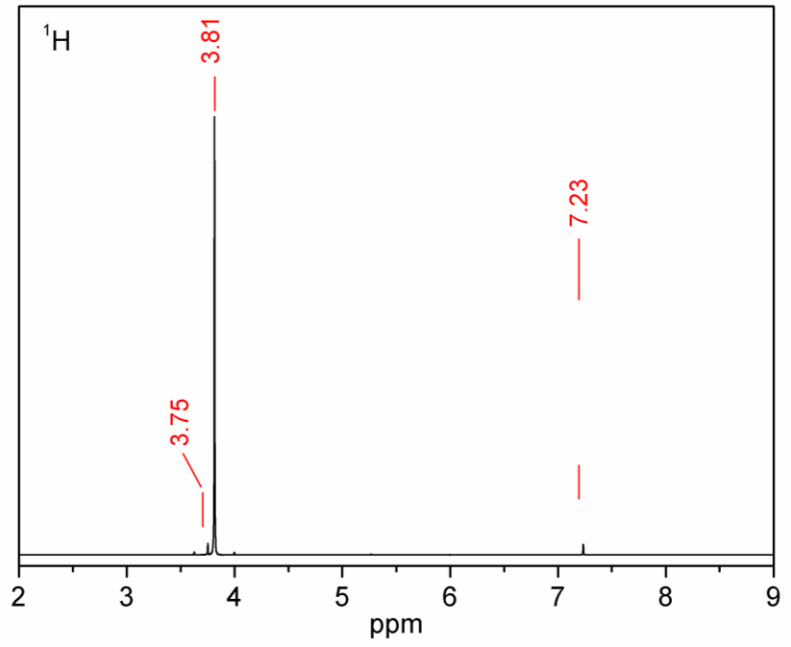

Figure S1. The ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, TMS, 298 K) of $CH_3OC(O)N_3$.

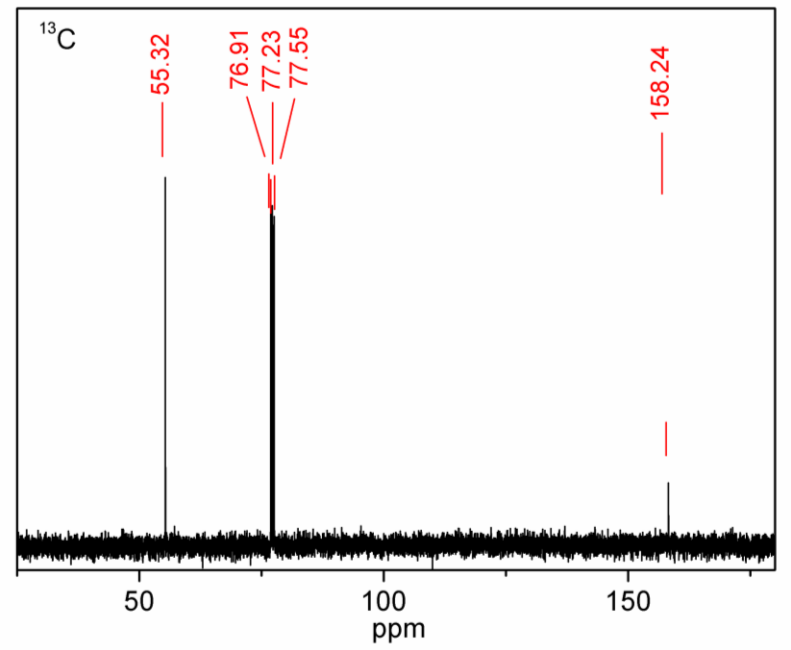

Figure S2. The ^{13}C NMR spectrum ($CDCl_3$, 400 MHz, TMS, 298 K) of $CH_3OC(O)N_3$.

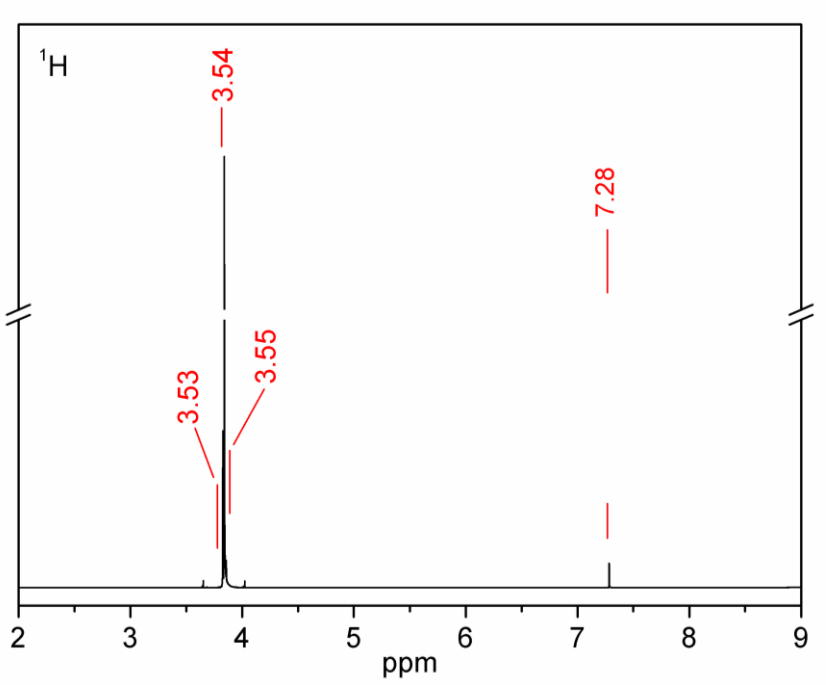

Figure S3. The ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, TMS, 298 K) of $CH_3OC(O)NCO$.

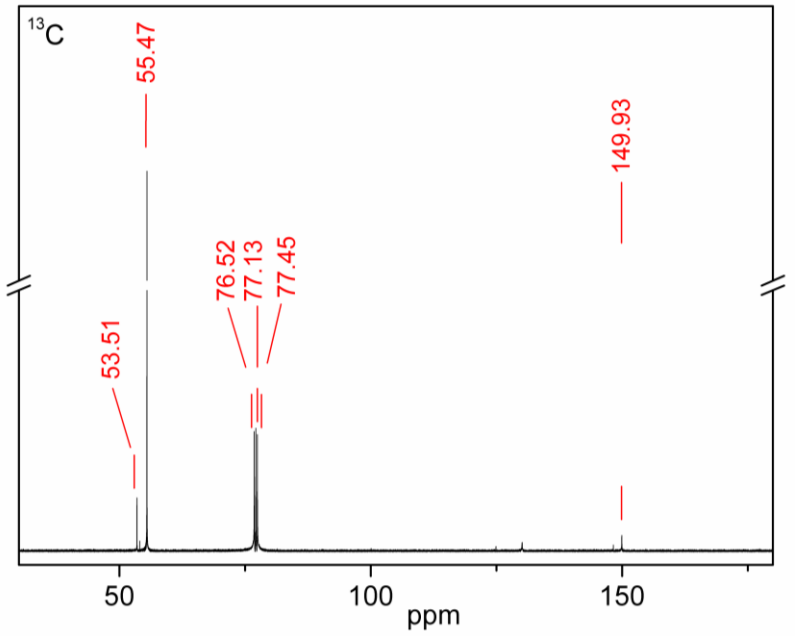

Figure S4. The ^{13}C NMR spectrum ($CDCl_3$, 400 MHz, TMS, 298 K) of $CH_3OC(O)NCO$.

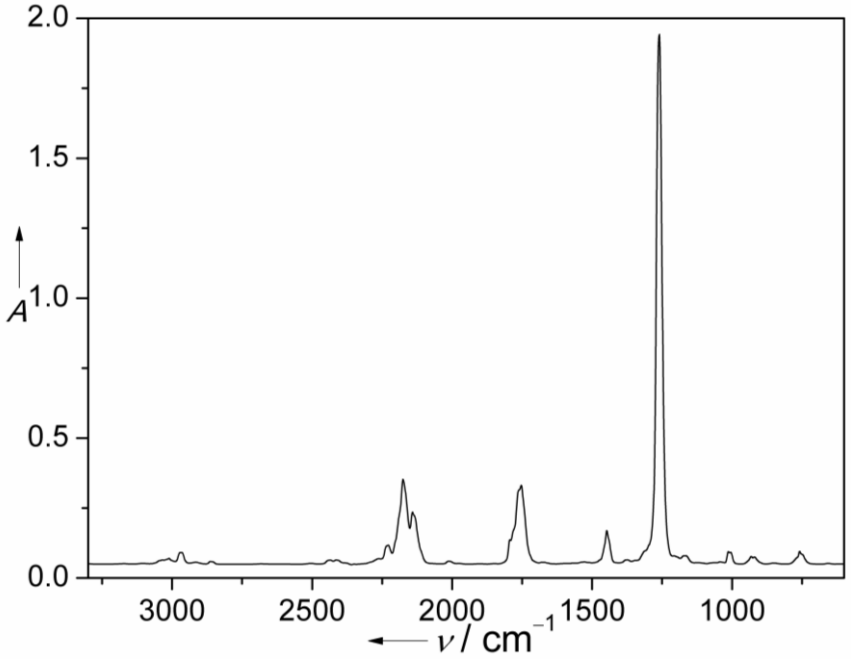

Figure S5. The IR spectrum of gaseous $CH_3OC(O)N_3$ at 298 K (Absorption *A*, resolution 2 cm^{-1}).

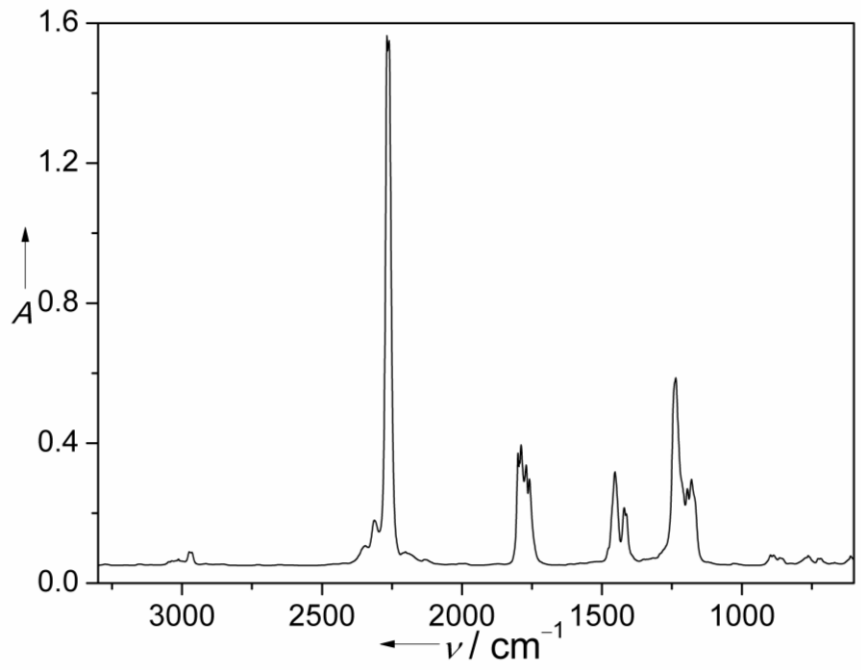

Figure S6. The IR spectrum of gaseous $CH_3OC(O)NCO$ at 298 K (Absorption *A*, resolution 2 cm^{-1}).

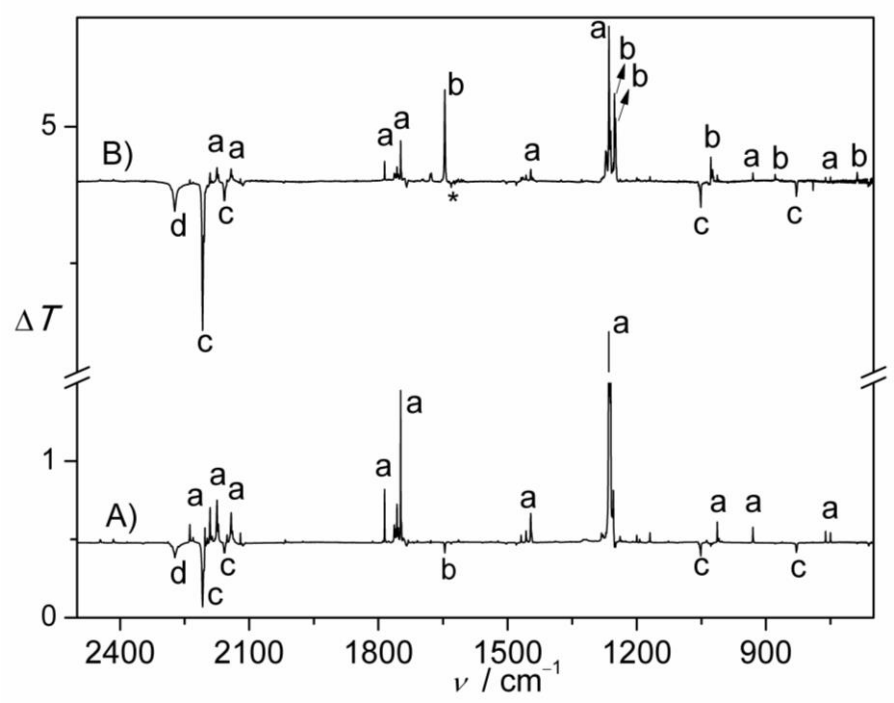

Figure S7. A) IR difference spectrum showing the change of Ne-matrix isolated $CH_3OC(O)N_3$ upon 266 nm laser photolysis; B) IR difference spectrum showing the change the matrix after subsequent 365 nm light irradiation; The IR bands of $CH_3OC(O)N_3$ (a), *syn*-$CH_3OC(O)N$ (b), CH_3ONCO (c), HNCO (d) and H_2O (*) are labelled. Bands for the depleted species point upward and bands for the formed species point downward.

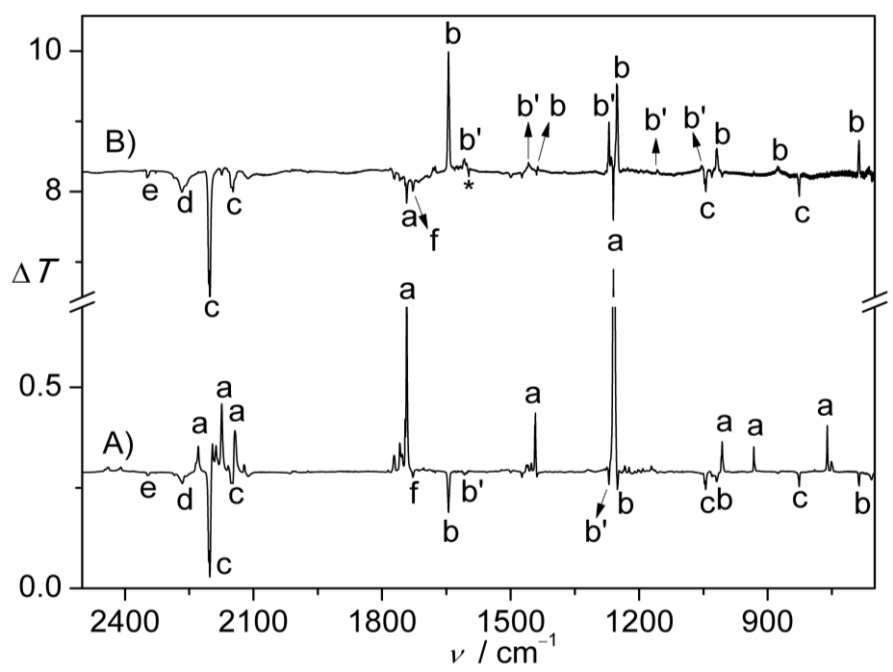

Figure S8. A) IR difference spectrum showing the change of N_2-matrix isolated $CH_3OC(O)N_3$ upon 193 nm laser photolysis; B) IR difference spectrum showing the change the matrix after subsequent 365 nm light irradiation; The IR bands of $CH_3OC(O)N_3$ (a), *syn*-$CH_3OC(O)N$ (b), *anti*-$CH_3OC(O)N$ (b'), CH_3ONCO (c), HNCO (d), CO_2 (e), H_2CO (f) and H_2O (*) are labelled. Bands for the depleted species point upward and bands for the formed species point downward.

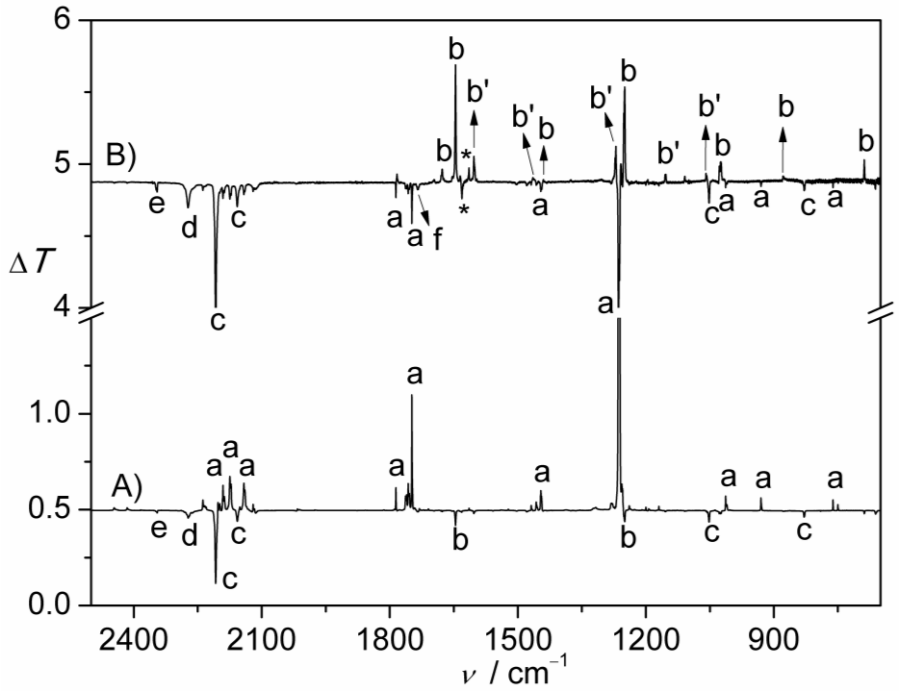

Figure S9. A) IR difference spectrum showing the change of Ne-matrix isolated $CH_3OC(O)N_3$ upon 193 nm laser photolysis; B) IR difference spectrum showing the change the matrix after subsequent 365 nm light irradiation; The IR bands of $CH_3OC(O)N_3$ (a), *syn*-$CH_3OC(O)N$ (b), *anti*-$CH_3OC(O)N$ (b'), CH_3ONCO (c), HNCO (d), CO_2 (e), H_2CO (f) and H_2O (*) are labelled. Bands for the depleted species point upward and bands for the formed species point downward.

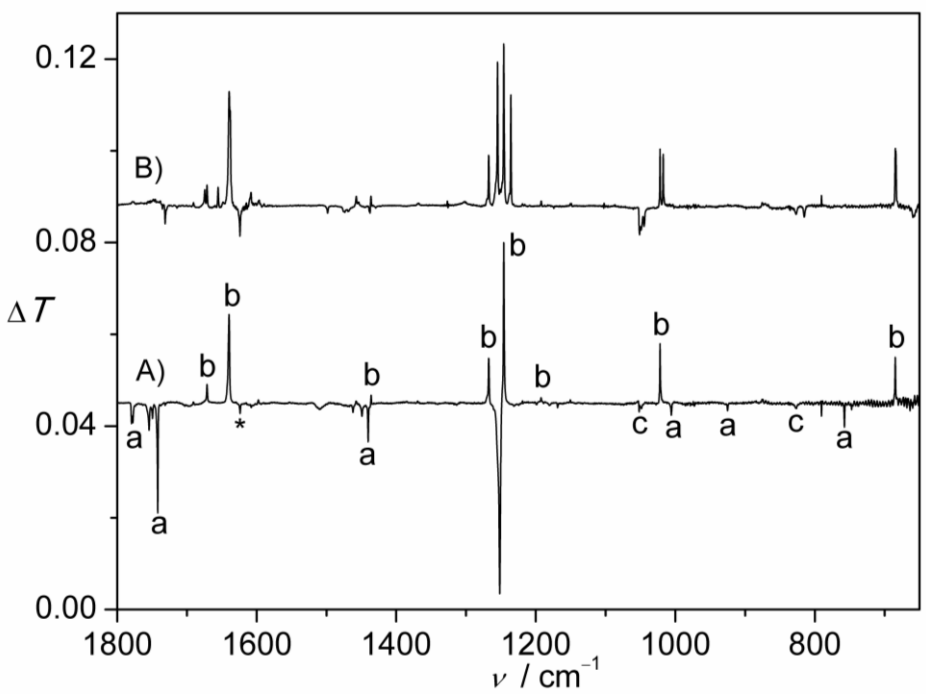

Figure S10. A) IR difference spectrum showing the change of Ar-matrix isolated photolysis (266 nm) products of $CH_3OC(O)N_3$ upon subsequent 365 nm light irradiation; B) IR difference spectrum showing the change of Ar-matrix isolated photolysis (266 nm) products of ^{15}N-labelled $CH_3OC(O)N_3$ upon subsequent 365 nm light irradiation; The IR bands of $CH_3OC(O)N_3$ (a), *syn*-$CH_3OC(O)N$ (b), CH_3ONCO (c) and H_2O (*) are labelled. Bands for the depleted species point upward and bands for the formed species point downward.

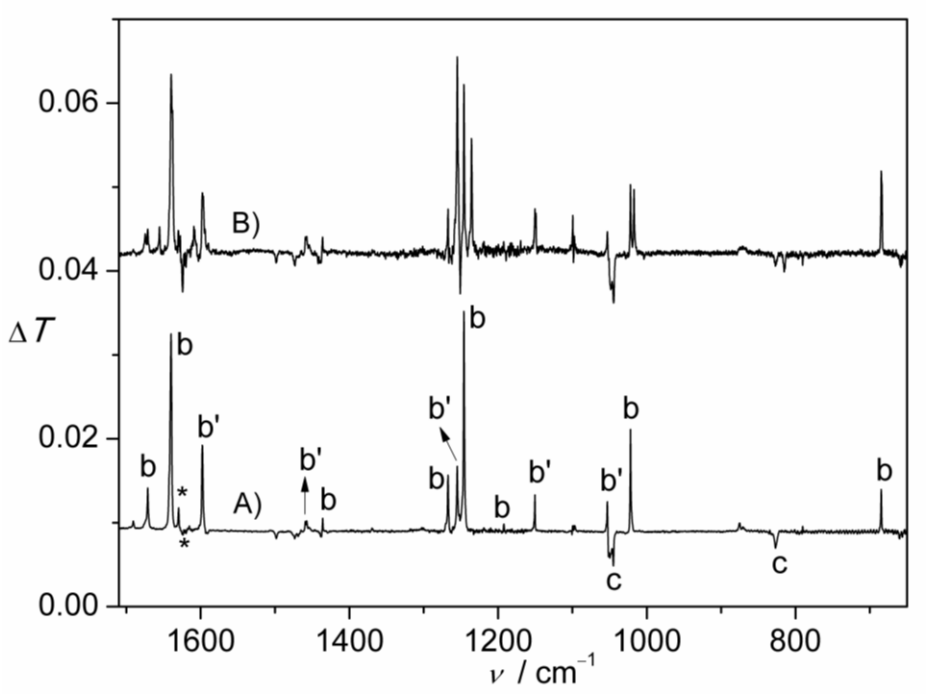

Figure S11. A) IR difference spectrum showing the change of Ar-matrix isolated photolysis (193 nm) products of $CH_3OC(O)N_3$ upon subsequent 365 nm light irradiation; B) IR difference spectrum showing the change of Ar-matrix isolated photolysis (193 nm) products of ^{15}N-labelled $CH_3OC(O)N_3$ upon subsequent 365 nm light irradiation; The IR bands of *syn*-$CH_3OC(O)N$ (b), *anti*-$CH_3OC(O)N_3$ (b'), CH_3ONCO (c) and H_2O (*) are labelled. Bands for the depleted species point upward and bands for the formed species point downward.

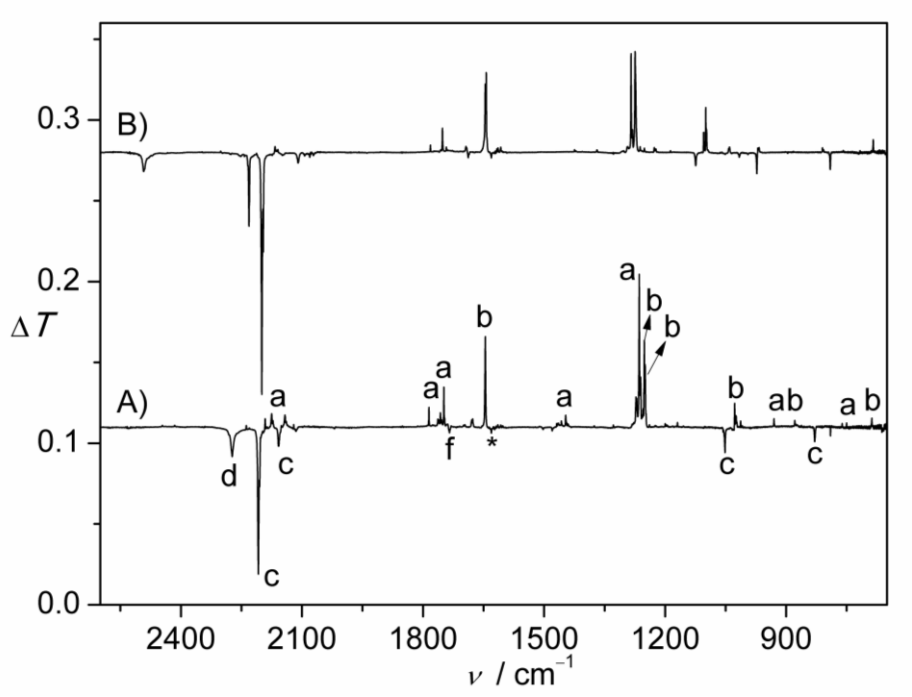

Figure S 12. A) IR difference spectrum showing the change of Ne-matrix isolated photolysis (266 nm) products of $CH_3OC(O)N_3$ upon subsequent 365 nm light irradiation; B) IR difference spectrum showing the change of Ne-matrix isolated photolysis (266 nm) products of $CD_3OC(O)N_3$ upon subsequent 365 nm light irradiation; The IR bands of $CH_3OC(O)N_3$ (a), *syn*-$CH_3OC(O)N$ (b), CH_3ONCO (c), HNCO (d), H_2CO (f) and H_2O (*) are labelled. Bands for the depleted species point upward and bands for the formed species point downward.

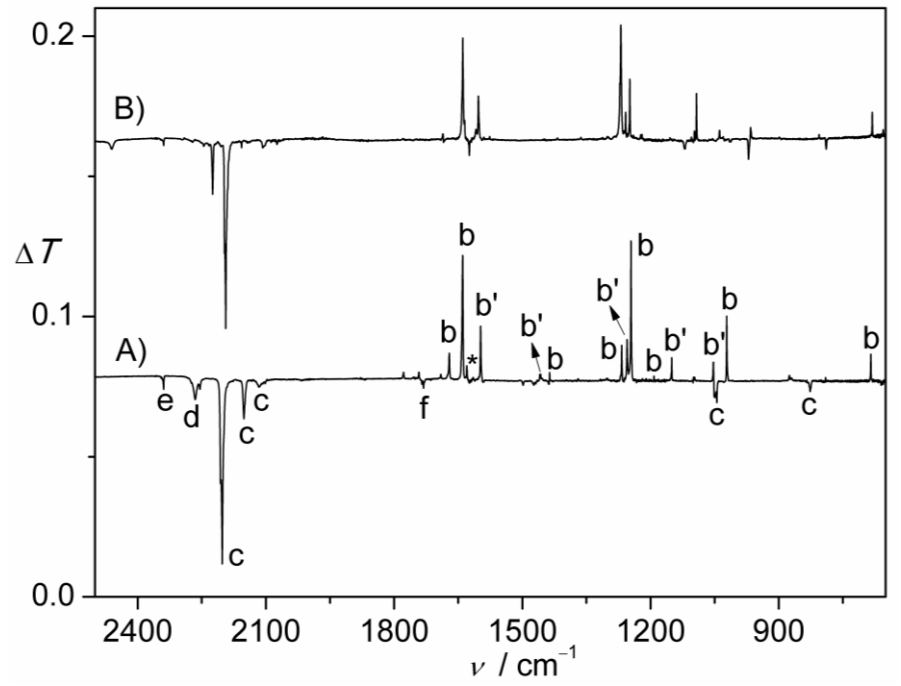

Figure S13. A) IR difference spectrum showing the change of Ar-matrix isolated photolysis (193 nm) products of $CH_3OC(O)N_3$ upon subsequent 365 nm light irradiation; B) IR difference spectrum showing the change of Ar-matrix isolated photolysis (193 nm) products of $CD_3OC(O)N_3$ upon subsequent 365 nm light irradiation; The IR bands of *syn*-$CH_3OC(O)N$ (b), *anti*-$CH_3OC(O)N_3$ (b'), CH_3ONCO (c), and HNCO (d), CO_2 (e), H_2CO (f) and H_2O (*) are labelled. Bands for the depleted species point upward and bands for the formed species point downward.

Table S1. TD-DFT B3LYP/6-311++G(3df,3pd) calculated vertical transitions (> 190 nm) of $CH_3OC(O)N$.

$CH_3OC(O)N$							
syn conformer (b)				*anti* conformer (b')			
singlet		triplet		singlet		triplet	
energy (nm)	oscillator strength	energy (nm)	oscillator strength	energy (nm)	oscillator strength	energy (nm)	oscillator strength
689	0.0003	406	**0.0099**	642	0.0004	465	**0.0053**
251	0.0002	363	**0.0072**	236	0.0012	389	**0.0140**
232	0.0009	316	**0.0037**	209	0.0212	340	**0.0023**
220	0.0150	291	0.0004	198	0.0045	320	**0.0003**
198	0.0016	245	0.0107			253	0.0126
		241	0.0007			234	0.0028
		213	0.0315			218	0.0156
		196	0.0053			194	0.0011

Table S2. The calculated IR frequencies (cm^{-1}) and IR intensities (km mol^{-1}) of $CH_3OC(O)N$ at the B3LYP/6-311++G(3df,3pd) level.

$CH_3OC(O)N$			
syn conformer (b)		*anti* conformer (b')	
singlet	triplet	singlet	triplet
3178 (4)	3171 (8)	3178 (4)	3163 (7)
3146 (9)	3132 (11)	3134 (10)	1326 (13)
3065 (17)	3057 (16)	3056 (17)	3051 (24)
1804 (387)	1664 (214)	1799 (400)	1625 (241)
1499 (19)	1494 (7)	1499 (13)	1499 (10)
1493 (11)	1486 (10)	1495 (12)	1497 (20)
1474 (4)	1470 (4)	1470 (9)	1478 (1)
1391 (69)	1265 (272)	1405 (70)	1275 (264)
1210 (34)	1212 (8)	1222 (34)	1173 (1)
1173 (1)	1172 (1)	1175 (1)	1170 (63)
1091 (127)	1039 (54)	1091 (92)	1070 (46)
887 (9)	882 (12)	902 (28)	842 (24)
653 (27)	700 (37)	654 (27)	665 (41)
599 (1)	639 (5)	583 (2)	573 (7)
417 (20)	423 (18)	440 (10)	477 (15)
247 (6)	271 (5)	232 (6)	275 (3)
141 (1)	170 (1)	155 (<1)	149 (1)
60 (<1)	122 (<1)	91 (<1)	124 (<1)

Table S3. Calculated free energies (Hartree) and relative energies (kcal mol^{-1}) of $CH_3OC(O)N$

Free Energies (Hartree)				
Method	*syn* conformer (b)		*anti* conformer (b')	
	singlet	triplet	singlet	triplet
B3LYP/6-311++G(3df,3pd)	-283.166881	-283.186573	-283.166667	-283.180326
BP86/6-311++G(3df,3pd)	-283.180641	-283.190024	-283.180571	-283.184753
M06-2X/6-311++G(3df,3pd)	-283.046164	-283.069148	-283.045798	-283.063319
CBS-QB3	-282.733393	-282.743293	-282.733139	-282.736741
Relative Energies (kcal mol^{-1})				
B3LYP/6-311++G(3df,3pd)	12.36	0	12.49	3.92
BP86/6-311++G(3df,3pd)	5.89	0	5.93	3.31
M06-2X/6-311++G(3df,3pd)	14.42	0	14.65	3.66
CBS-QB3	6.21	0	6.37	4.11

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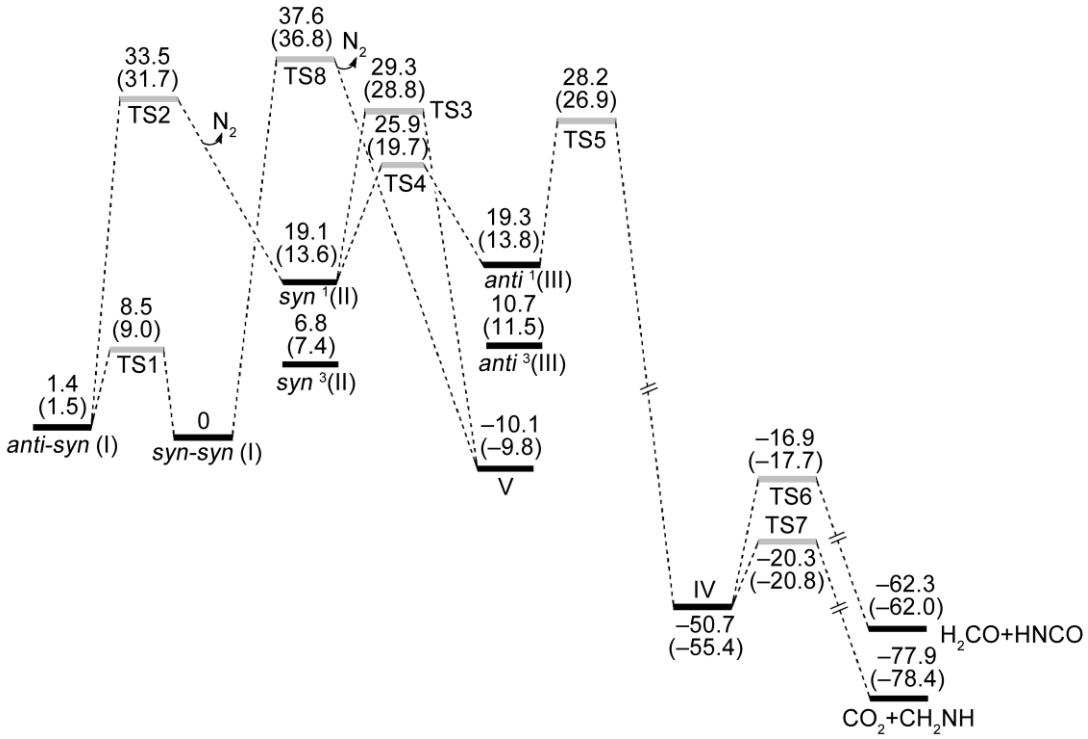

Figure S14. Calculated relative energies (kcal mol^{-1}) of the minima and transition states for the decomposition of *anti-syn* and *syn-syn* conformer of $CH_3OC(O)N_3$ at B3LYP/6-311++G(3df,3pd) level of theory. The relative energies calculated at the CBS-QB3 level are given in parentheses. For the molecular structures (I-V) and transition states (TS1-TS8) see Figure S15 and Figure S16.

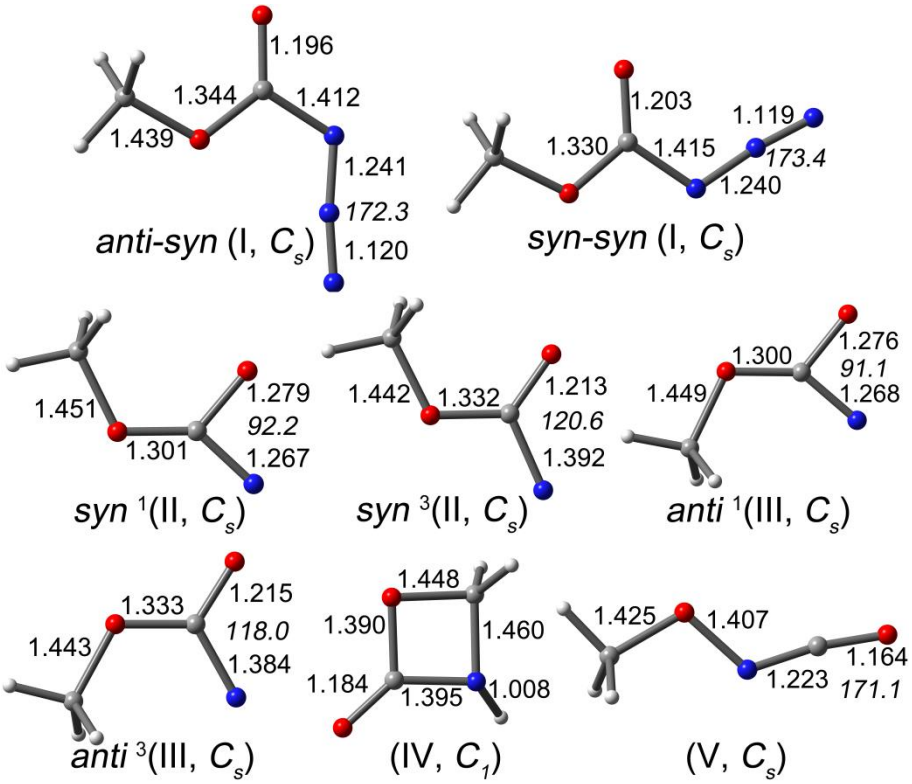

Figure S15. Optimized structures of minima on the singlet PES of (I) at the B3LYP/6-311++G(3df,3pd) level of theory. Bond lengths are given in [Å]. Nitrogen, carbon, and oxygen atoms are shown in blue, grey and red respectively. Molecular symmetries are shown in parentheses.

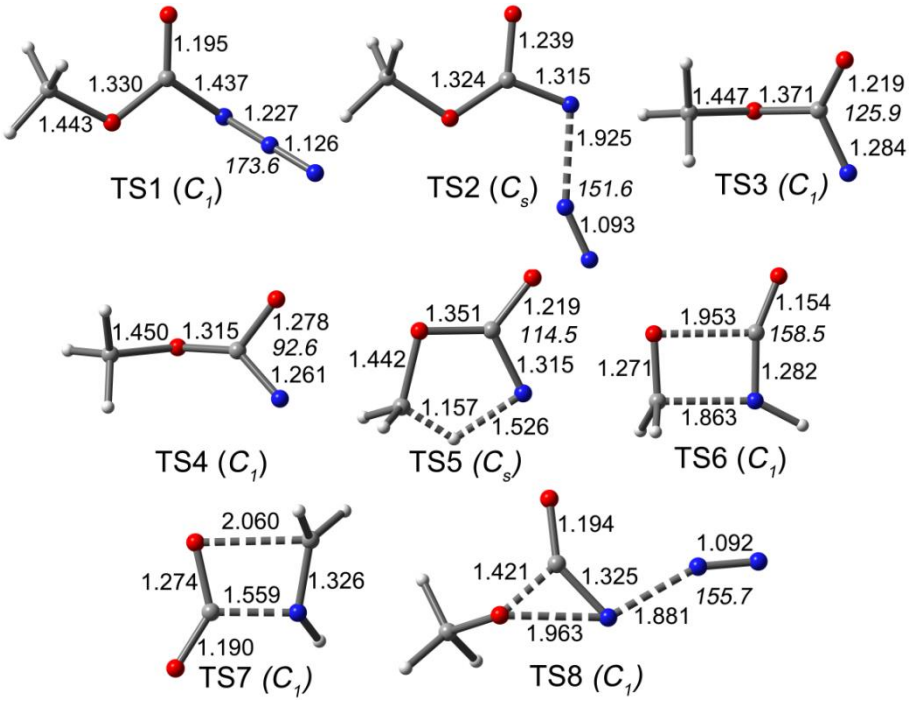

Figure S16. Optimized structures of transition states (TS) on the singlet PES of (I) with the B3LYP/6-311++G(3df,3pd) method. Bond lengths are given in [Å]. Nitrogen, carbon, and oxygen atoms are shown in blue, grey and red respectively. Molecular symmetries are shown in parentheses.

Calculated energies (in Hartree, at 298 K) and atomic coordinates (in Angstroms) for all optimized structures at the B3LYP/6-311++G(3df,3pd) and CBS-QB3 levels of theory using the Gaussian 09 software package

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***syn-syn* $CH_3OC(O)N_3$**

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.065544 (Hartree/Particle)
Thermal correction to Energy=	0.072434
Thermal correction to Enthalpy=	0.073378
Thermal correction to Gibbs Free Energy=	0.034116
Sum of electronic and zero-point Energies=	-392.746174
Sum of electronic and thermal Energies=	-392.739283
Sum of electronic and thermal Enthalpies=	-392.738339
Sum of electronic and thermal Free Energies=	-392.777601

C	0.000000	0.308836	0.000000
O	-0.976898	1.211674	0.000000
C	-0.545429	2.583277	0.000000
H	0.046931	2.793455	0.887541
H	0.046931	2.793455	-0.887541
H	-1.457595	3.169992	0.000000
N	-0.603123	-0.971601	0.000000
O	1.180972	0.536231	0.000000
N	0.203251	-1.913910	0.000000
N	0.828975	-2.842035	0.000000

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.064814	E(Thermal)=	0.071780
E(SCF)=	-390.623753	DE(MP2)=	-1.374654
DE(CBS)=	-0.131865	DE(MP34)=	-0.013646
DE(CCSD)=	-0.042718	DE(Int)=	0.041840
DE(Empirical)=	-0.060417		
CBS-QB3 (0 K)=	-392.140398	CBS-QB3 Energy=	-392.133432
CBS-QB3 Enthalpy=	-392.132488	CBS-QB3 Free Energy=	-392.171959

***anti-syn* $CH_3OC(O)N_3$**

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.065433 (Hartree/Particle)
Thermal correction to Energy=	0.072292
Thermal correction to Enthalpy=	0.073236
Thermal correction to Gibbs Free Energy=	0.033974
Sum of electronic and zero-point Energies=	-392.743840
Sum of electronic and thermal Energies=	-392.736981
Sum of electronic and thermal Enthalpies=	-392.736037
Sum of electronic and thermal Free Energies=	-392.775299

C	0.000000	0.739852	0.000000
O	-0.939765	-0.220698	0.000000
C	-2.301556	0.245095	0.000000
H	-2.494396	0.842536	0.888020
H	-2.494396	0.842536	-0.888020
H	-2.912090	-0.651576	0.000000
N	1.308496	0.210225	0.000000
O	-0.203369	1.918377	0.000000
N	1.423235	-1.025387	0.000000
N	1.676167	-2.116927	0.000000

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.064686	E(Thermal)=	0.071623
E(SCF)=	-390.619318	DE(MP2)=	-1.376972
DE(CBS)=	-0.131918	DE(MP34)=	-0.012945
DE(CCSD)=	-0.043050	DE(Int)=	0.041894
DE(Empirical)=	-0.060365		
CBS-QB3 (0 K)=	-392.137987	CBS-QB3 Energy=	-392.131050
CBS-QB3 Enthalpy=	-392.130106	CBS-QB3 Free Energy=	-392.169579

***syn*- $CH_3OC(O)N$ ($^1A'$)**

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.053602 (Hartree/Particle)
Thermal correction to Energy=	0.059128
Thermal correction to Enthalpy=	0.060073
Thermal correction to Gibbs Free Energy=	0.024586
Sum of electronic and zero-point Energies=	-283.137865
Sum of electronic and thermal Energies=	-283.132338
Sum of electronic and thermal Enthalpies=	-283.131394
Sum of electronic and thermal Free Energies=	-283.166881

C	0.000000	0.546578	0.000000
O	0.894260	-0.398073	0.000000
C	0.380266	-1.755556	0.000000
H	-0.214850	-1.929422	0.892886
H	-0.214850	-1.929422	-0.892886
H	1.260871	-2.387022	0.000000
N	0.000000	1.814047	0.000000
O	-1.278391	0.498249	0.000000

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.052993	E(Thermal)=	0.058576
E(SCF)=	-281.613646	DE(MP2)=	-0.968937
DE(CBS)=	-0.095012	DE(MP34)=	-0.031520
DE(CCSD)=	-0.033652	DE(Int)=	0.030371
DE(Empirical)=	-0.044635		
CBS-QB3 (0 K)=	-282.704037	CBS-QB3 Energy=	-282.698454
CBS-QB3 Enthalpy=	-282.697510	CBS-QB3 Free Energy=	-282.733393

***syn*- $CH_3OC(O)N$ ($^3A''$)**

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.053232 (Hartree/Particle)
Thermal correction to Energy=	0.058521
Thermal correction to Enthalpy=	0.059465
Thermal correction to Gibbs Free Energy=	0.023825
Sum of electronic and zero-point Energies=	-283.157166
Sum of electronic and thermal Energies=	-283.151878
Sum of electronic and thermal Enthalpies=	-283.150933
Sum of electronic and thermal Free Energies=	-283.186573

C	0.000000	0.588827	0.000000
O	0.680298	-0.555951	0.000000
C	-0.111930	-1.760828	0.000000
H	-0.739098	-1.796226	0.888225
H	-0.739098	-1.796226	-0.888225
H	0.603329	-2.575536	0.000000
N	0.822432	1.711496	0.000000
O	-1.206620	0.708391	0.000000

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.052642	E(Thermal)=	0.057973
E(SCF)=	-281.698155	DE(MP2)=	-0.895531
DE(CBS)=	-0.091521	DE(MP34)=	-0.038827
DE(CCSD)=	-0.027098	DE(Int)=	0.027877
DE(Empirical)=	-0.043190		
CBS-QB3 (0 K)=	-282.713803	CBS-QB3 Energy=	-282.708472
CBS-QB3 Enthalpy=	-282.707528	CBS-QB3 Free Energy=	-282.743293

***anti*- $CH_3OC(O)N$ ($^1A'$)**

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.053720 (Hartree/Particle)
Thermal correction to Energy=	0.059163
Thermal correction to Enthalpy=	0.060108
Thermal correction to Gibbs Free Energy=	0.025068
Sum of electronic and zero-point Energies=	-283.138015
Sum of electronic and thermal Energies=	-283.132572
Sum of electronic and thermal Enthalpies=	-283.131628
Sum of electronic and thermal Free Energies=	-283.166667

C	0.000000	0.478979	0.000000
O	0.740352	-0.589388	0.000000
C	0.015469	-1.844243	0.000000
H	0.776180	-2.615817	0.000000
H	-0.600420	-1.916766	0.894048
H	-0.600420	-1.916766	-0.894048
N	-1.220457	0.821239	0.000000
O	0.369030	1.700921	0.000000

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.053141	E(Thermal)=	0.058597
E(SCF)=	-281.610777	DE(MP2)=	-0.975403
DE(CBS)=	-0.095193	DE(MP34)=	-0.029182
DE(CCSD)=	-0.032988	DE(Int)=	0.030441
DE(Empirical)=	-0.044551		
CBS-QB3 (0 K)=	-282.704511	CBS-QB3 Energy=	-282.699055
CBS-QB3 Enthalpy=	-282.698111	CBS-QB3 Free Energy=	-282.733139

***anti*- $CH_3OC(O)N$ ($^3A''$)**

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.052925 (Hartree/Particle)
Thermal correction to Energy=	0.058252
Thermal correction to Enthalpy=	0.059196
Thermal correction to Gibbs Free Energy=	0.023459
Sum of electronic and zero-point Energies=	-283.150860
Sum of electronic and thermal Energies=	-283.145533
Sum of electronic and thermal Enthalpies=	-283.144589
Sum of electronic and thermal Free Energies=	-283.180326

C	0.000000	0.608851	0.000000
O	0.718591	-0.514270	0.000000
C	0.027003	-1.780489	0.000000
H	0.809755	-2.531185	0.000000
H	-0.588311	-1.884646	0.891679
H	-0.588311	-1.884646	-0.891679
N	-1.382452	0.539424	0.000000
O	0.516661	1.708562	0.000000

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.052364	E(Thermal)=	0.057695
E(SCF)=	-281.689132	DE(MP2)=	-0.891031
DE(CBS)=	-0.091617	DE(MP34)=	-0.041980
DE(CCSD)=	-0.029873	DE(Int)=	0.027659
DE(Empirical)=	-0.043691		
CBS-QB3 (0 K)=	-282.707301	CBS-QB3 Energy=	-282.701970
CBS-QB3 Enthalpy=	-282.701026	CBS-QB3 Free Energy=	-282.736741

IV

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.057362 (Hartree/Particle)
Thermal correction to Energy=	0.061475
Thermal correction to Enthalpy=	0.062419
Thermal correction to Gibbs Free Energy=	0.030539
Sum of electronic and zero-point Energies=	-283.251284
Sum of electronic and thermal Energies=	-283.247172
Sum of electronic and thermal Enthalpies=	-283.246227
Sum of electronic and thermal Free Energies=	-283.278108

C	0.599268	-0.011387	-0.020651
O	-0.319828	1.030765	-0.011023
C	-1.384548	0.050514	0.039668
H	-2.070688	0.158420	-0.797436
H	-0.344282	-1.865736	0.389218
H	-1.899403	0.069340	0.999702
N	-0.381633	-0.997620	-0.122637
O	1.782014	0.017554	0.030132

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.056804	E(Thermal)=	0.060944
E(SCF)=	-281.740752	DE(MP2)=	-0.973991
DE(CBS)=	-0.095800	DE(MP34)=	-0.020370
DE(CCSD)=	-0.026957	DE(Int)=	0.029866
DE(Empirical)=	-0.045303		
CBS-QB3 (0 K)=	-282.816502	CBS-QB3 Energy=	-282.812362
CBS-QB3 Enthalpy=	-282.811418	CBS-QB3 Free Energy=	-282.843346

CH_3ONCO

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.054129 (Hartree/Particle)
Thermal correction to Energy=	0.059654
Thermal correction to Enthalpy=	0.060599
Thermal correction to Gibbs Free Energy=	0.025316
Sum of electronic and zero-point Energies=	-283.184667
Sum of electronic and thermal Energies=	-283.179141
Sum of electronic and thermal Enthalpies=	-283.178197
Sum of electronic and thermal Free Energies=	-283.213480

O	-0.758797	-0.750175	0.000000
C	-2.139391	-0.398264	0.000000
H	-2.395844	0.171556	0.893766
H	-2.395844	0.171556	-0.893766
H	-2.663581	-1.350841	0.000000
N	0.000000	0.434707	0.000000
C	1.222003	0.380525	0.000000
O	2.378747	0.509077	0.000000

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.053547	E(Thermal)=	0.059101
E(SCF)=	-281.659693	DE(MP2)=	-0.975235
DE(CBS)=	-0.095299	DE(MP34)=	-0.021829
DE(CCSD)=	-0.028947	DE(Int)=	0.030360
DE(Empirical)=	-0.044755		
CBS-QB3 (0 K)=	-282.741850	CBS-QB3 Energy=	-282.736296
CBS-QB3 Enthalpy=	-282.735352	CBS-QB3 Free Energy=	-282.770713

TS1

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.065212 (Hartree/Particle)
Thermal correction to Energy=	0.071355
Thermal correction to Enthalpy=	0.072300
Thermal correction to Gibbs Free Energy=	0.034640
Sum of electronic and zero-point Energies=	-392.733415
Sum of electronic and thermal Energies=	-392.727272
Sum of electronic and thermal Enthalpies=	-392.726328
Sum of electronic and thermal Free Energies=	-392.763987

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.330253
C	1.301709	0.000000	1.952613
H	1.855612	-0.890577	1.664957
H	1.856931	0.886200	1.654399
H	1.108618	0.006387	3.019648
N	-1.349407	0.097589	-0.485143
O	0.961944	-0.000525	-0.708302
N	-1.952356	-0.951622	-0.690120
N	-2.600072	-1.842764	-0.922663

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.064452	E(Thermal)=	0.070687
E(SCF)=	-390.605189	DE(MP2)=	-1.379930
DE(CBS)=	-0.132091	DE(MP34)=	-0.012577
DE(CCSD)=	-0.043261	DE(Int)=	0.042041
DE(Empirical)=	-0.060288		
CBS-QB3 (0 K)=	-392.126844	CBS-QB3 Energy=	-392.120608
CBS-QB3 Enthalpy=	-392.119664	CBS-QB3 Free Energy=	-392.157574

TS2

B3LYP/6-311++G(3df,3pd

Zero-point correction=	0.060695 (Hartree/Particle)
Thermal correction to Energy=	0.068578
Thermal correction to Enthalpy=	0.069522
Thermal correction to Gibbs Free Energy=	0.027390
Sum of electronic and zero-point Energies=	-392.690979
Sum of electronic and thermal Energies=	-392.683096
Sum of electronic and thermal Enthalpies=	-392.682152
Sum of electronic and thermal Free Energies=	-392.724283

C	0.000000	0.740520	0.000000
O	-1.072124	-0.036382	0.000000
C	-2.333619	0.666167	0.000000
H	-2.421474	1.285115	0.889819
H	-2.421474	1.285115	-0.889819
H	-3.090847	-0.110168	0.000000
N	1.253707	0.343552	0.000000
O	0.035413	1.978570	0.000000
N	1.268597	-1.581660	0.000000
N	1.796154	-2.538705	0.000000

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.059956	E(Thermal)=	0.067955
E(SCF)=	-390.586085	DE(MP2)=	-1.332263
DE(CBS)=	-0.128447	DE(MP34)=	-0.036542
DE(CCSD)=	-0.045413	DE(Int)=	0.041509
DE(Empirical)=	-0.060310		
CBS-QB3 (0 K)=	-392.087594	CBS-QB3 Energy=	-392.079594
CBS-QB3 Enthalpy=	-392.078650	CBS-QB3 Free Energy=	-392.121487

TS3

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.052007 (Hartree/Particle)
Thermal correction to Energy=	0.057216
Thermal correction to Enthalpy=	0.058160
Thermal correction to Gibbs Free Energy=	0.023231
Sum of electronic and zero-point Energies=	-283.121852
Sum of electronic and thermal Energies=	-283.116643
Sum of electronic and thermal Enthalpies=	-283.115699
Sum of electronic and thermal Free Energies=	-283.150628

C	-0.634905	0.000000	-0.074848
O	0.616423	0.259098	-0.572526
C	1.726082	-0.129787	0.270628
H	1.663726	0.386666	1.227291
H	1.708662	-1.207372	0.417048
H	2.621564	0.171192	-0.261713
N	-1.147077	1.139618	0.235407
O	-1.180357	-1.080262	0.046882

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.051395	E(Thermal)=	0.056667
E(SCF)=	-281.607708	DE(MP2)=	-0.935655
DE(CBS)=	-0.093673	DE(MP34)=	-0.039957
DE(CCSD)=	-0.039587	DE(Int)=	0.029902
DE(Empirical)=	-0.044961		
CBS-QB3 (0 K)=	-282.680243	CBS-QB3 Energy=	-282.674970
CBS-QB3 Enthalpy=	-282.674026	CBS-QB3 Free Energy=	-282.709260

TS4

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.053039 (Hartree/Particle)
Thermal correction to Energy=	0.057864
Thermal correction to Enthalpy=	0.058808
Thermal correction to Gibbs Free Energy=	0.025106
Sum of electronic and zero-point Energies=	-283.128189
Sum of electronic and thermal Energies=	-283.123364
Sum of electronic and thermal Enthalpies=	-283.122420
Sum of electronic and thermal Free Energies=	-283.156123

C	0.497838	-0.052565	-0.147009
O	-0.720909	0.060037	-0.627570
C	-1.806944	-0.014658	0.330980
H	-2.712858	0.100600	-0.252906
H	-1.799152	-0.981550	0.830073
H	-1.719567	0.793627	1.054599
N	1.307825	-0.978371	0.130089
O	1.337338	0.857371	0.171794

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.052427	E(Thermal)=	0.057296
E(SCF)=	-281.599987	DE(MP2)=	-0.973036
DE(CBS)=	-0.095294	DE(MP34)=	-0.031163
DE(CCSD)=	-0.034520	DE(Int)=	0.030512
DE(Empirical)=	-0.044545		
CBS-QB3 (0 K)=	-282.695606	CBS-QB3 Energy=	-282.690737
CBS-QB3 Enthalpy=	-282.689793	CBS-QB3 Free Energy=	-282.723618

TS5

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.051180 (Hartree/Particle)
Thermal correction to Energy=	0.055753
Thermal correction to Enthalpy=	0.056698
Thermal correction to Gibbs Free Energy=	0.023642
Sum of electronic and zero-point Energies=	-283.124941
Sum of electronic and thermal Energies=	-283.120368
Sum of electronic and thermal Enthalpies=	-283.119424
Sum of electronic and thermal Free Energies=	-283.152480

C	0.000000	0.557083	0.000000
O	0.905716	-0.445353	0.000000
C	0.098094	-1.615682	0.000000
H	0.236746	-2.188739	0.912702
H	-1.012492	-1.289683	0.000000
H	0.236746	-2.188739	-0.912702
N	-1.269486	0.214771	0.000000
O	0.198888	1.759773	0.000000

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.050333	E(Thermal)=	0.055097
E(SCF)=	-281.596511	DE(MP2)=	-0.957488
DE(CBS)=	-0.095217	DE(MP34)=	-0.034455
DE(CCSD)=	-0.036141	DE(Int)=	0.030216
DE(Empirical)=	-0.044707		
CBS-QB3 (0 K)=	-282.683971	CBS-QB3 Energy=	-282.679206
CBS-QB3 Enthalpy=	-282.678261	CBS-QB3 Free Energy=	-282.712244

TS6

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.051960 (Hartree/Particle)
Thermal correction to Energy=	0.056902
Thermal correction to Enthalpy=	0.057847
Thermal correction to Gibbs Free Energy=	0.024064
Sum of electronic and zero-point Energies=	-283.196389
Sum of electronic and thermal Energies=	-283.191446
Sum of electronic and thermal Enthalpies=	-283.190502
Sum of electronic and thermal Free Energies=	-283.224285

C	0.000000	0.792658	0.000000
O	0.876218	-0.952259	0.000000
C	-0.284507	-1.470490	0.000000
H	-0.704110	-1.892408	0.921499
H	-1.959905	0.782735	0.000000
H	-0.704110	-1.892408	-0.921499
N	-1.131350	0.188865	0.000000
O	0.748158	1.670764	0.000000

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.051494	E(Thermal)=	0.056448
E(SCF)=	-281.665634	DE(MP2)=	-0.983422
DE(CBS)=	-0.096865	DE(MP34)=	-0.017077
DE(CCSD)=	-0.029964	DE(Int)=	0.030875
DE(Empirical)=	-0.044761		
CBS-QB3 (0 K)=	-282.755355	CBS-QB3 Energy=	-282.750400
CBS-QB3 Enthalpy=	-282.749456	CBS-QB3 Free Energy=	-282.783312

TS7

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.053904 (Hartree/Particle)
Thermal correction to Energy=	0.058349
Thermal correction to Enthalpy=	0.059294
Thermal correction to Gibbs Free Energy=	0.026601
Sum of electronic and zero-point Energies=	-283.202466
Sum of electronic and thermal Energies=	-283.198021
Sum of electronic and thermal Enthalpies=	-283.197076
Sum of electronic and thermal Free Energies=	-283.229769

C	0	-0.625824	0.064293	0.015726
O	0	-0.084115	1.208450	-0.125233
C	0	1.573994	0.000000	0.079386
H	0	1.705355	0.622345	0.950878
H	0	0.616045	-1.609924	-0.663438
H	0	2.392834	-0.034804	-0.635215
N	0	0.601353	-0.897546	0.054214
O	0	-1.742476	-0.345703	0.049934

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.053169	E(Thermal)=	0.057711
E(SCF)=	-281.671252	DE(MP2)=	-0.980764
DE(CBS)=	-0.096473	DE(MP34)=	-0.019698
DE(CCSD)=	-0.031531	DE(Int)=	0.030605
DE(Empirical)=	-0.044858		
CBS-QB3 (0 K)=	-282.760803	CBS-QB3 Energy=	-282.756260
CBS-QB3 Enthalpy=	-282.755316	CBS-QB3 Free Energy=	-282.788200

TS8

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.060385 (Hartree/Particle)
Thermal correction to Energy=	0.068189
Thermal correction to Enthalpy=	0.069133
Thermal correction to Gibbs Free Energy=	0.027337
Sum of electronic and zero-point Energies=	-392.684558
Sum of electronic and thermal Energies=	-392.676754
Sum of electronic and thermal Enthalpies=	-392.675810
Sum of electronic and thermal Free Energies=	-392.717605

C	0	0.354885	0.380801	-0.206228
O	0	1.534576	-0.323948	-0.569831
C	0	2.495133	-0.431220	0.497371
H	0	2.755560	0.564301	0.853534
H	0	2.089742	-1.032446	1.310532
H	0	3.363054	-0.923216	0.069218
N	0	-0.357858	-0.734700	-0.251103
O	0	0.260758	1.546997	0.033893
N	0	-2.116623	-0.152593	0.074201
N	0	-3.192824	-0.268496	0.220811

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.059742	E(Thermal)=	0.067584
E(SCF)=	-390.578048	DE(MP2)=	-1.336453
DE(CBS)=	-0.128988	DE(MP34)=	-0.033632
DE(CCSD)=	-0.044191	DE(Int)=	0.041647
DE(Empirical)=	-0.060240		
CBS-QB3 (0 K)=	-392.080163	CBS-QB3 Energy=	-392.072321
CBS-QB3 Enthalpy=	-392.071376	CBS-QB3 Free Energy=	-392.113284

***syn-syn* $CH_3OC(O)NCO$**

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.065958 (Hartree/Particle)
Thermal correction to Energy=	0.072890
Thermal correction to Enthalpy=	0.073834
Thermal correction to Gibbs Free Energy=	0.034167
Sum of electronic and zero-point Energies=	-396.642562
Sum of electronic and thermal Energies=	-396.635630
Sum of electronic and thermal Enthalpies=	-396.634686
Sum of electronic and thermal Free Energies=	-396.674353

C	0.000031834	-0.000013464	-0.000014556
O	-0.000022681	0.000022072	-0.000006924
C	0.000013364	0.000010788	0.000026247
H	-0.000000228	-0.000004667	-0.000006982
H	0.000000239	-0.000005164	-0.000010863
H	-0.000003169	0.000000665	-0.000009942
N	-0.000054252	-0.000007429	-0.000084541
C	0.000102687	0.000062175	0.000172962
O	-0.000055907	-0.000041955	-0.000085215
O	-0.000011888	-0.000023021	0.000019813

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.065312	E(Thermal)=	0.072302
E(SCF)=	-394.542281	DE(MP2)=	-1.342298
DE(CBS)=	-0.131427	DE(MP34)=	-0.020058
DE(CCSD)=	-0.038879	DE(Int)=	0.041304
DE(Empirical)=	-0.061486		
CBS-QB3 (0 K)=	-396.029814	CBS-QB3 Energy=	-396.022824
CBS-QB3 Enthalpy=	-396.021879	CBS-QB3 Free Energy=	-396.061698

***syn-anti* $CH_3OC(O)NCO$**

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.065730 (Hartree/Particle)
Thermal correction to Energy=	0.072678
Thermal correction to Enthalpy=	0.073622
Thermal correction to Gibbs Free Energy=	0.033838
Sum of electronic and zero-point Energies=	-396.636494
Sum of electronic and thermal Energies=	-396.629545
Sum of electronic and thermal Enthalpies=	-396.628601
Sum of electronic and thermal Free Energies=	-396.668385

C	-0.000094363	0.000036741	0.000133177
O	0.000029336	-0.000009032	-0.000105264
C	0.000009342	-0.000002011	-0.000013623
H	-0.000004756	0.000011829	0.000008639
H	0.000008781	-0.000000465	0.000028930
H	-0.000003650	-0.000011499	0.000009245
N	0.000064156	-0.000008947	0.000023615
C	-0.000062744	-0.000002334	0.000020079
O	0.000058617	0.000000791	-0.000055894
O	-0.000004718	-0.000015073	-0.000048904

CBS-QB3

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.065077	E(Thermal)=	0.072061
E(SCF)=	-394.534741	DE(MP2)=	-1.343423
DE(CBS)=	-0.131398	DE(MP34)=	-0.020119
DE(CCSD)=	-0.038864	DE(Int)=	0.041318
DE(Empirical)=	-0.061451		
CBS-QB3 (0 K)=	-396.023600	CBS-QB3 Energy=	-396.016616
CBS-QB3 Enthalpy=	-396.015672	CBS-QB3 Free Energy=	-396.055519

***anti-syn* $CH_3OC(O)NCO$**

B3LYP/6-311++G(3df,3pd)

Zero-point correction=	0.065816 (Hartree/Particle)
Thermal correction to Energy=	0.072762
Thermal correction to Enthalpy=	0.073707
Thermal correction to Gibbs Free Energy=	0.033852
Sum of electronic and zero-point Energies=	-396.641379
Sum of electronic and thermal Energies=	-396.634433
Sum of electronic and thermal Enthalpies=	-396.633488
Sum of electronic and thermal Free Energies=	-396.673343

C	0.000222165	-0.000197854	-0.000069256
O	-0.000175745	0.000118194	0.000018773
C	0.000026325	-0.000029283	0.000001945
H	0.000003058	0.000004434	0.000007020
H	0.000005160	0.000004831	-0.000007387
H	0.000017078	0.000015617	0.000000584
N	-0.000072408	-0.000053351	0.000017966
O	-0.000024710	0.000085058	0.000027667
C	-0.000036658	-0.000023063	0.000004164
O	0.000035736	0.000075416	-0.000001477

CBS

Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.065141	E(Thermal)=	0.072153
E(SCF)=	-394.540713	DE(MP2)=	-1.342935
DE(CBS)=	-0.131420	DE(MP34)=	-0.019963
DE(CCSD)=	-0.039030	DE(Int)=	0.041308
DE(Empirical)=	-0.061465		
CBS-QB3 (0 K)=	-396.029077	CBS-QB3 Energy=	-396.022064
CBS-QB3 Enthalpy=	-396.021120	CBS-QB3 Free Energy=	-396.061158