Supporting information

Phosphenic isocyanate (O_2PNCO): Gas-phase generation, characterization, and photodecomposition reactions

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Experimental and computational details

Sample preparation

Caution! Covalent azides are highly energetic and may decompose explosively. Especially, $C_2H_4O_2PN_3$ undergoes fast hydrolysis when exposing to moisture by forming highly toxic and explosive hydrazoic acid (HN_3). Although no explosion was encountered with purified $C_2H_4O_2PN_3$ during this work, it should be handled with great care in small quantities (< 5 mmol) and appropriate safety precautions (face shields, leather gloves, and protective clothes) should be taken. Ignoring safety precautions may lead to serious injuries!

2-Isocyanato-1,3,2-dioxaphospholane, $C_2H_4O_2PNCO$, was synthesized by reaction of $C_2H_4O_2PCl$ (97%, Sigma-Aldrich) with AgNCO (98 %, Alfa Aesar). Briefly, commercial 2-chloro-1,3,2-dioxaphospholane (1 mmol, 0.09 mL) and dry silver isocyanate (1.5 mmol, 0.225 g) were added into a reaction vessel containing acetonitrile (1 mL) under inert atmosphere. The mixture was stirred 48 h at room temperature. The volatile products were separated by passing through three successive cold U-traps (–10, –35, and –196 °C). Pure $C_2H_4O_2PNCO$ was retained in the second trap, and its hydrolysis product HNCO was trapped in the last trap. The purity of the substance was checked with gas phase IR (INSA OPTICS FOLI10-R, ν = 2260, 1403, 1014, 926, 810, 756, and 690 cm^{-1}) and NMR spectroscopy (Bruker Avance III HD 500 spectrometer, ^{31}P NMR (162 MHz, CD_3CN): δ = –122.9 ppm). By analogy, 2-azido-1,3,2-dioxaphospholane, $C_2H_4O_2PN_3$, was synthesized by the reaction of $C_2H_4O_2PCl$ (97%, Sigma-Aldrich,1 mmol) with Me_3SiN_3 (95%, Aladdin, 6 mmol) in THF (2 mL). And its quality was checked with gas-phase IR spectroscopy (ν = 2130, 1262, 1014, 925, 852, 809, 757, and 720 cm^{-1}).

Gases Ar (≥ 99.999%, Linde), and N_2 (≥ 99.999%, Linde) were used without further purification.

Matrix-isolation IR spectroscopy

Matrix IR spectra were recorded on an FT-IR spectrometer (Bruker 70V) in a reflectance mode using a transfer optic. A KBr beam splitter and MCT detector were used in the mid-IR region (5000–400 cm^{-1}). Typically, 200 scans at a resolution of 0.5 cm^{-1} were co-added for each spectrum. Gaseous sample was mixed by passing through a flow of argon or nitrogen gas through a U-trap (–32 °C) containing ca. 20 mg of the freshly prepared precursor ($C_2H_4O_2PNCO$ or $C_2H_4O_2PN_3$). Then the mixture (sample : dilution gas = 1:1000, estimated) was passed through an Al_2O_3 tube furnace (o.d 2.0 mm, i.d. 1.0 mm), which can be heated over a length of ca. 25 mm by tantalum wire (o.d. 2.0 mm, resistance 0.4 Ω, voltage 7.50 V, and current 3.46 A). The resulting pyrolysis products were immediately deposited (2 mmol h^{-1}) in a high vacuum (~10^{-6} pa) onto the gold-plated copper block matrix support (10 K for N_2 and Ar matrix) using a closed-cycle helium cryostat (Sumitomo Heavy Industries, SRDK-408D2-F50H) inside the vacuum chamber. Temperatures at the second stage of the cold head were controlled using an East Changing TC 290 digital cryogenic temperature controller a Silicon Diode (DT-670). Photolysis experiments were performed using

ArF excimer laser (Gamlaser EX5/250, 193 nm, 3 Hz,), Nd^{3+}: YAG laser (MPL-F-266, 266 nm, 10 mW), and UV flashlight (Boyu, 365 nm, 24 W).

Matrix-isolation UV-vis spectroscopy

Matrix UV-vis spectra were recorded on a PerkinElmer Lambda 850+ spectrometer (190–800 nm, scanning speed of 1 nm s^{-1}). The high-vacuum flash pyrolysis products using the similar Al_2O_3 furnace (o.d 2.0 mm, i.d. 1.0 mm) were deposited onto a CaF_2 matrix support (10 K) using a closed-cycle helium cryostat (Sumitomo Heavy Industries, SRDK-408D2-F50H) inside the vacuum chamber. Temperatures at the second stage of the cold head were controlled using a Lake Shore 335 digital cryogenic temperature controller a Silicon Diode (DT-670).

Quantum chemical calculation methods

Structures and IR frequencies for stationary points were calculated using the (unrestricted) DFT B3LYP[1], BP86[2] and MPW1PW91[3] methods with the 6-311++G(3df, 3pd) basis set. Relative energies of the species were further estimated using the complete basis set (CBS-QB3).[4] Local minima were confirmed by vibrational frequency analysis, and transition states were ascertained with additional intrinsic reaction coordinate (IRC) calculations.[5] Time-dependent TD-B3LYP/6-311+G(3df)[6] method was performed for the calculation of the vertical excitation energies. All these computations were performed using the Gaussian 09 software package.[7] Further calculations on the single-point energies for all the species on the potential energy profiles were carried out at the (U)CCSD(T)-F12a/aug-cc-pVTZ[8] level. IR frequencies and intensities of O_2PNCO with configuration-selective vibrational configuration interaction theory (VCI)[9] analysis was obtained at the CCSD(T)-F12a/cc-pVTZ-F12 level. IR frequencies and intensities of O_2PN and OPNO with second-order vibrational perturbation theory (VPT2)[10] were obtained at the (U)CCSD(T)-F12a/cc-pVTZ-F12 level. All these ab initio calculations were preformed with the MOLPRO 2015 package.[11]

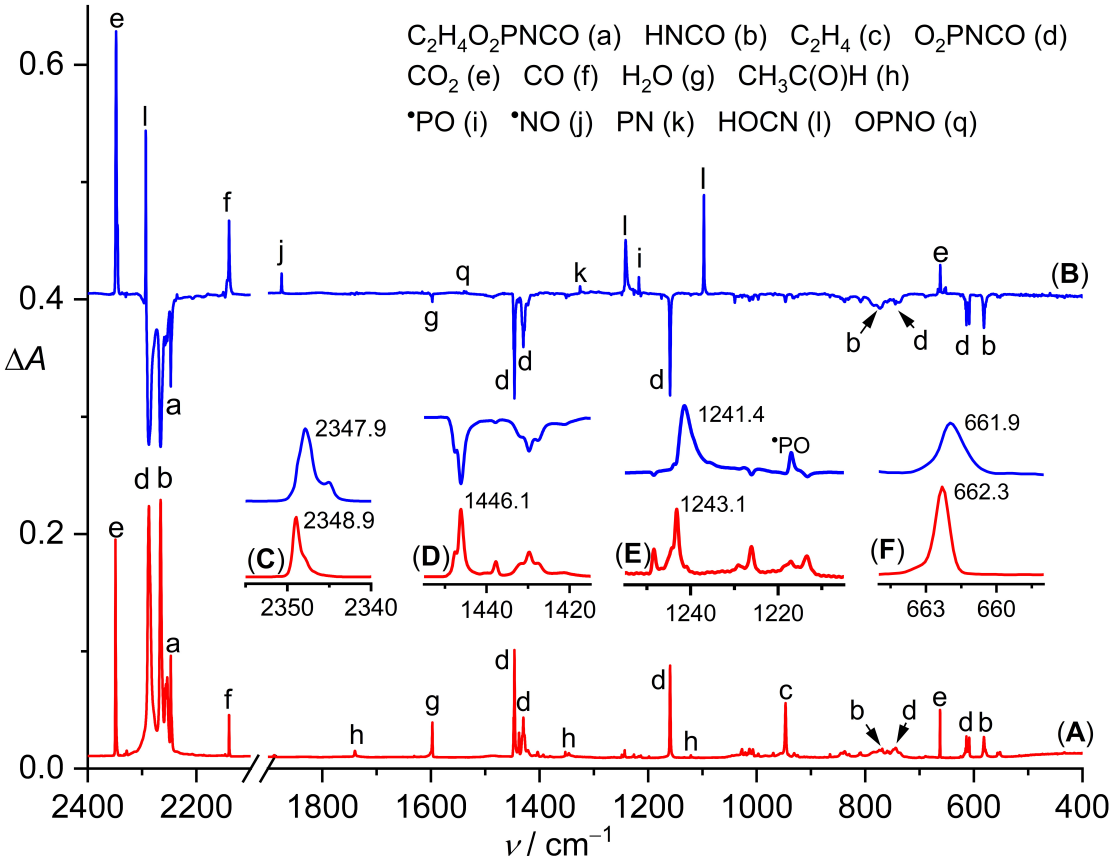

Figure S1. (A) IR spectrum of N_2-matrix isolated HVFP (ca. 1000 K) products of $C_2H_4O_2PNCO$ (**a**) at 10 K. (B) IR difference spectrum showing the change of N_2-matrix containing the HVFP products of **a** upon 193 nm laser irradiation (20 min) at 10 K. (C–F) Parts of the expanded IR spectra showing the shifts of the IR bands for CO_2 due to weak interaction with OPN in the matrix.

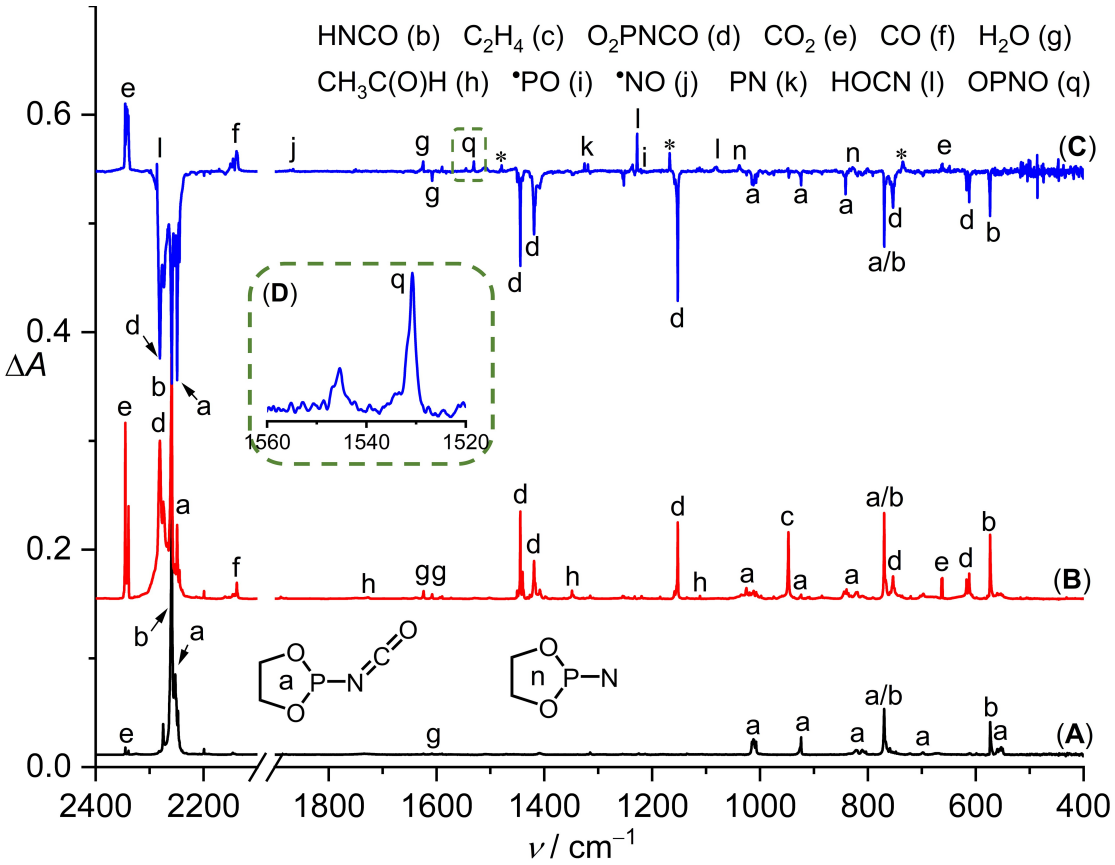

Figure S2. (A) IR spectrum of Ar-matrix isolated $C_2H_4O_2PNCO$ (**a**) at 10 K. (B) IR spectrum of Ar-matrix isolated high vacuum flash pyrolysis (HVFP, ca. 1000K) products of **a** at 10 K. (B) IR difference spectrum showing the change of Ar-matrix containing HVFP products of **a** upon 193 nm laser irradiation (4 min) at 10 K.

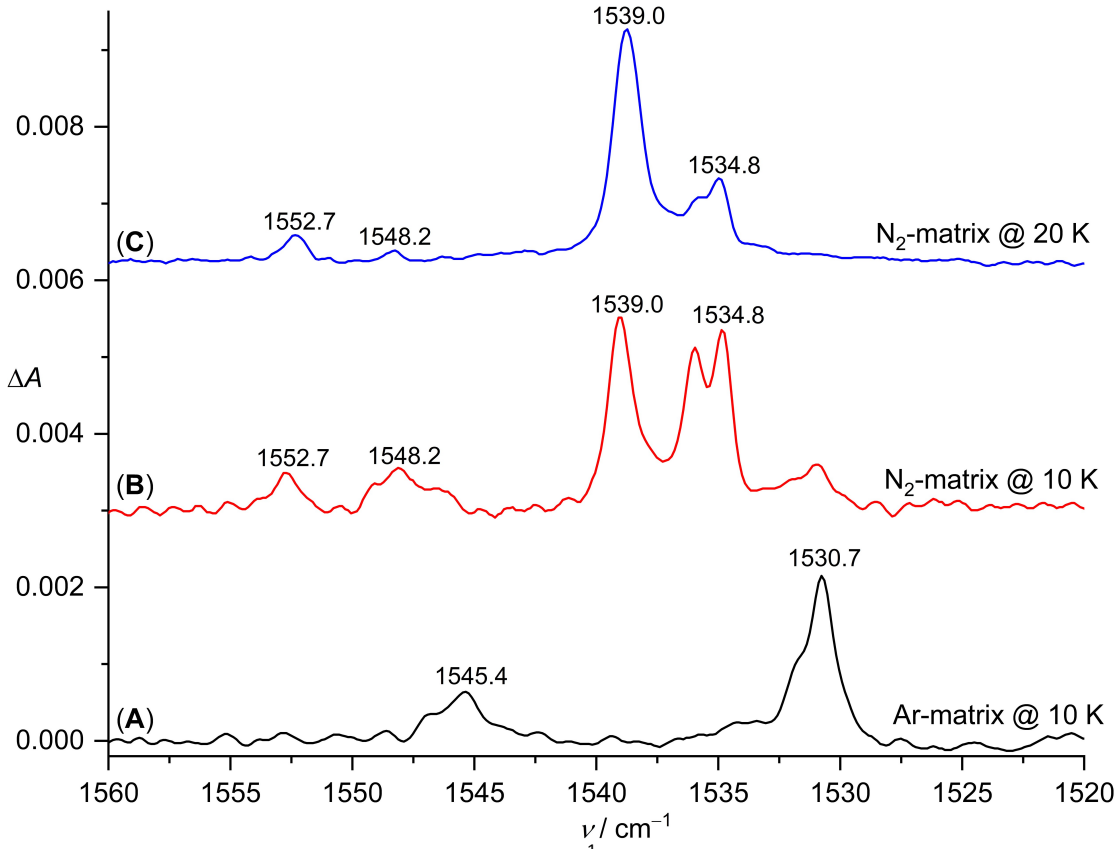

Figure S3. Parts of the IR spectra (1560–1520 cm^{-1}) showing the formation of OPNO during the photochemistry of O_2PNCO in Ar-matrix at 10 K (spectrum A), in N_2-matrix at 10 K (spectrum B), and in N_2-matrix at 20 K (spectrum C). For the experiment at 20 K, the N_2-matrix (10 K) containing the HVFP products of $C_2H_4O_2PNCO$ (**a**) was first warmed to 20 K, and then it was photolyzed with a 193 nm laser (4 min).

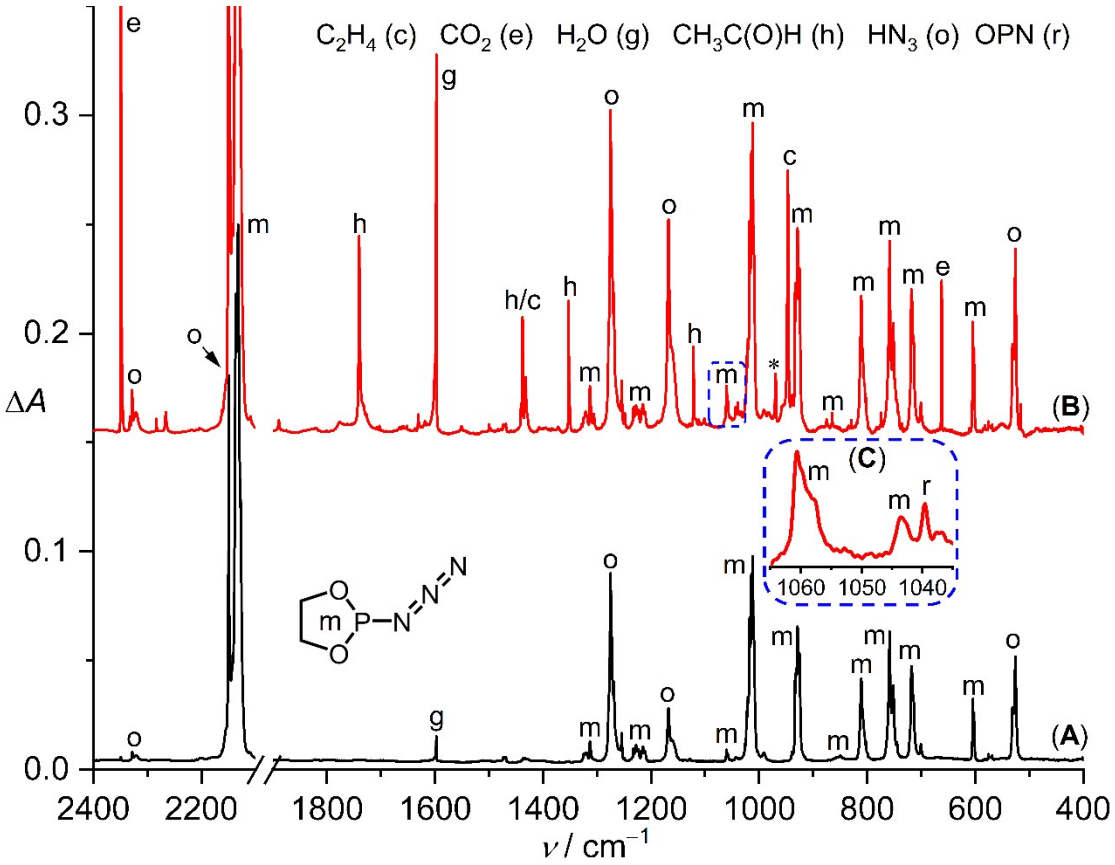

Figure S4. (A) IR spectrum of N_2-matrix isolated $C_2H_4O_2PN_3$ (**m**) at 10 K. (B) IR spectrum of N_2-matrix isolated HVFP (ca. 1000 K) products of **m** at 10 K. (C) Part of the expanded IR spectrum B in the range of 1065–1035 cm^{-1} showing the weak IR band of OPN.

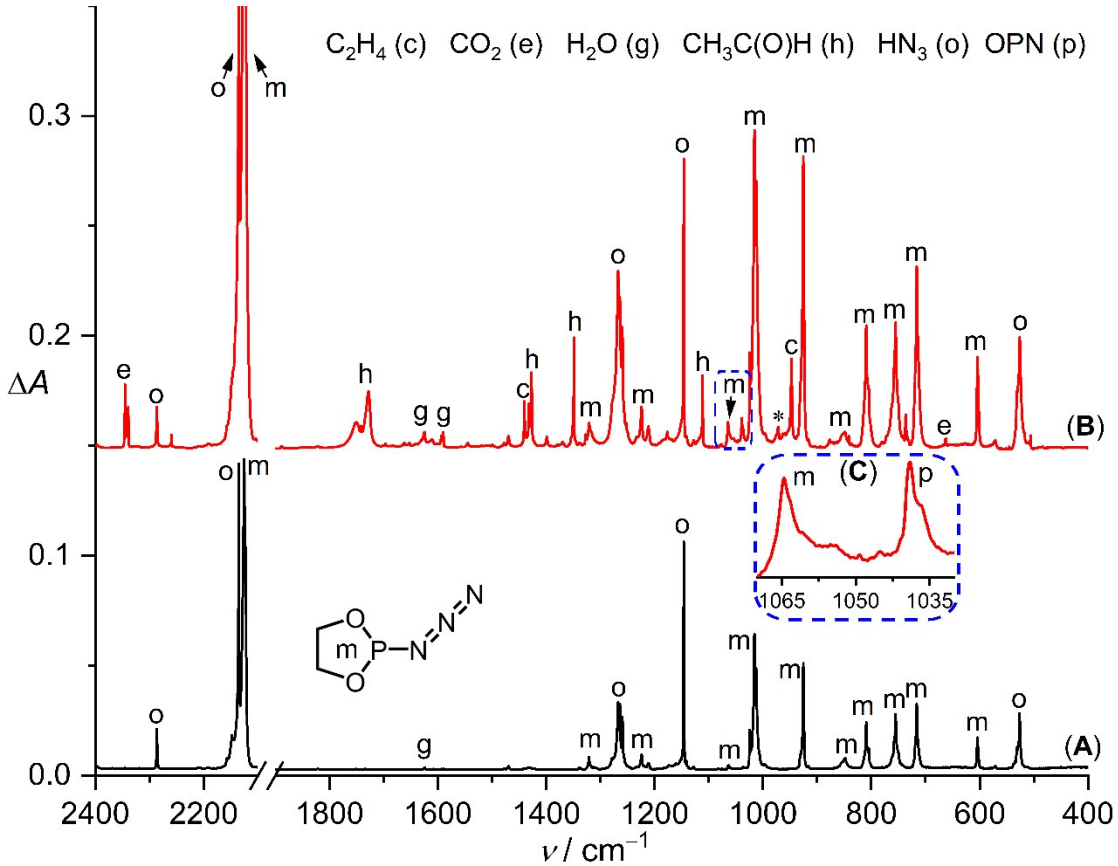

Figure S5. (A) IR spectrum of Ar-matrix isolated $C_2H_4O_2PN_3$ (**m**) at 10 K. (B) IR spectrum of Ar-matrix isolated HVFP (ca. 1000 K) products of **m** at 10 K. (C) Part of the expanded IR spectrum B in the range of 1070–1030 cm^{-1} showing the weak IR band of OPN.

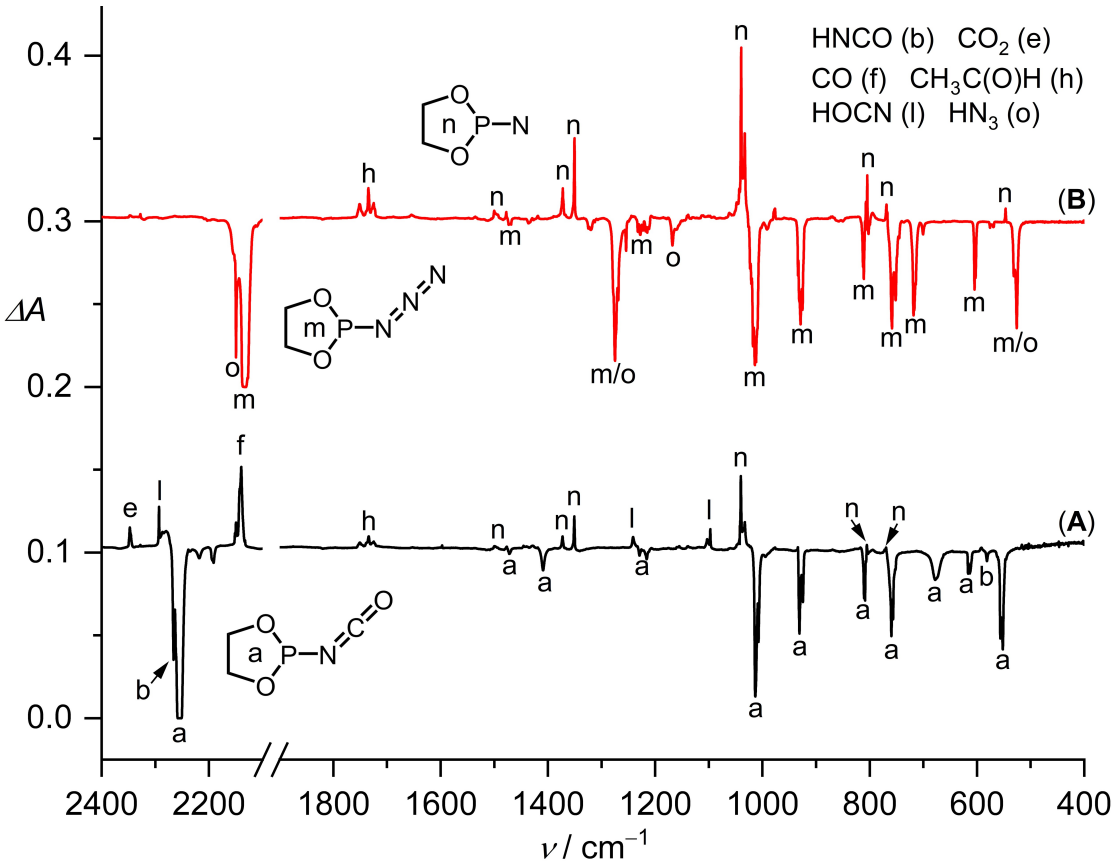

Figure S6. (A) IR difference spectrum showing the change of N_2-matrix isolated $C_2H_4O_2PNCO$ (**a**) upon irradiation at 193 nm (6 min) at 10 K. (A) IR difference spectrum showing the change of N_2-matrix isolated $C_2H_4O_2PN_3$ (**m**) upon irradiation at 193 nm (2 min) at 10 K.

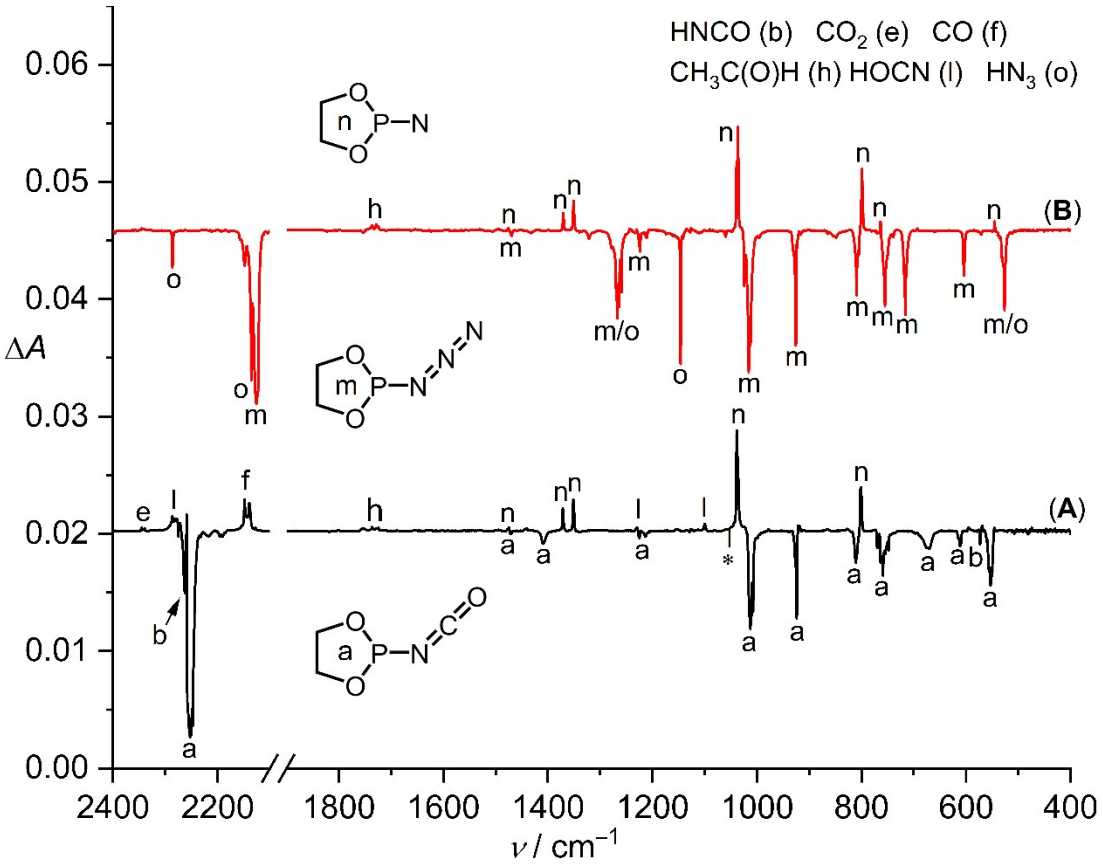

Figure S7. (A) IR difference spectrum showing the change of Ar-matrix isolated $C_2H_4O_2PNCO$ (**a**) upon 193 nm laser irradiation (4 min) at 10 K. (B) IR difference spectrum showing the change of Ar-matrix isolated $C_2H_4O_2PN_3$ (**m**) upon 193 nm laser irradiation (2 min) at 10 K.

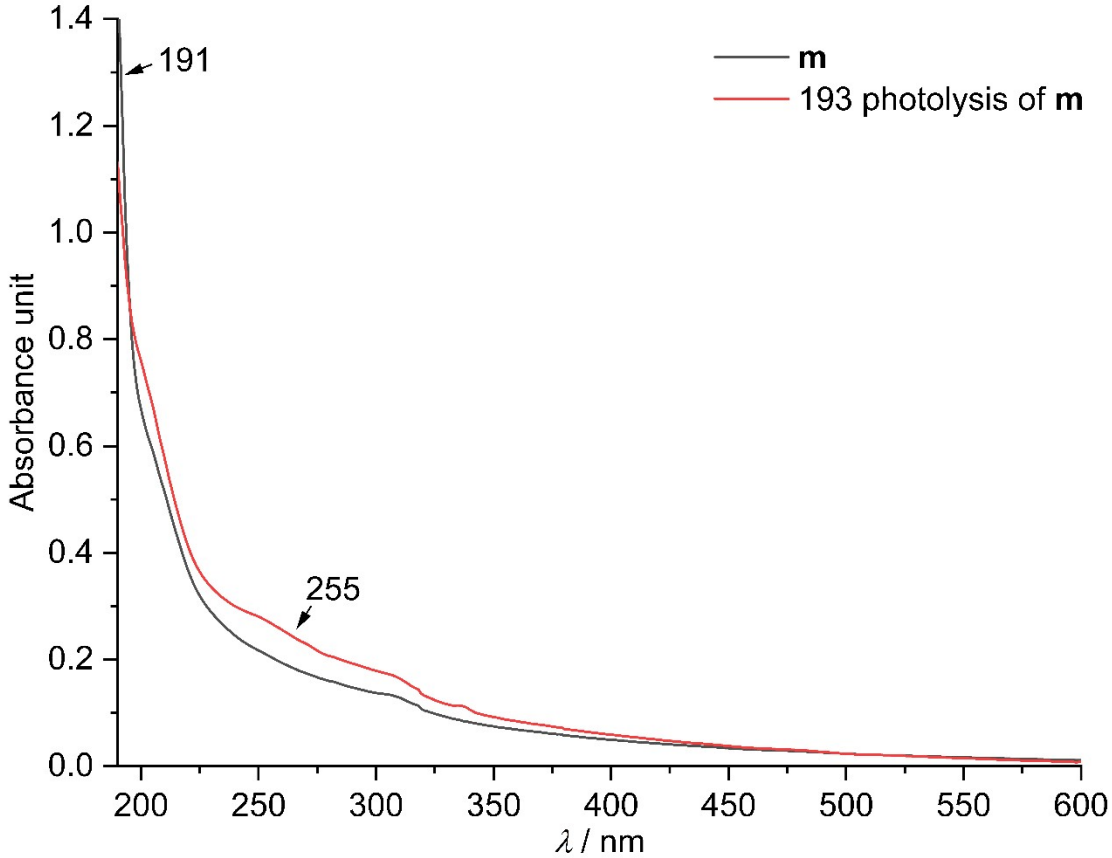

Figure S8. UV-Vis spectra of N_2-matrix isolated $C_2H_4O_2PN_3$ (**m**) and its laser photolysis (193 nm) products at 10 K. The increased broad absorption in the range of 200-450 nm is assinged to the nitrene intermediate $C_2H_4O_2PN$.

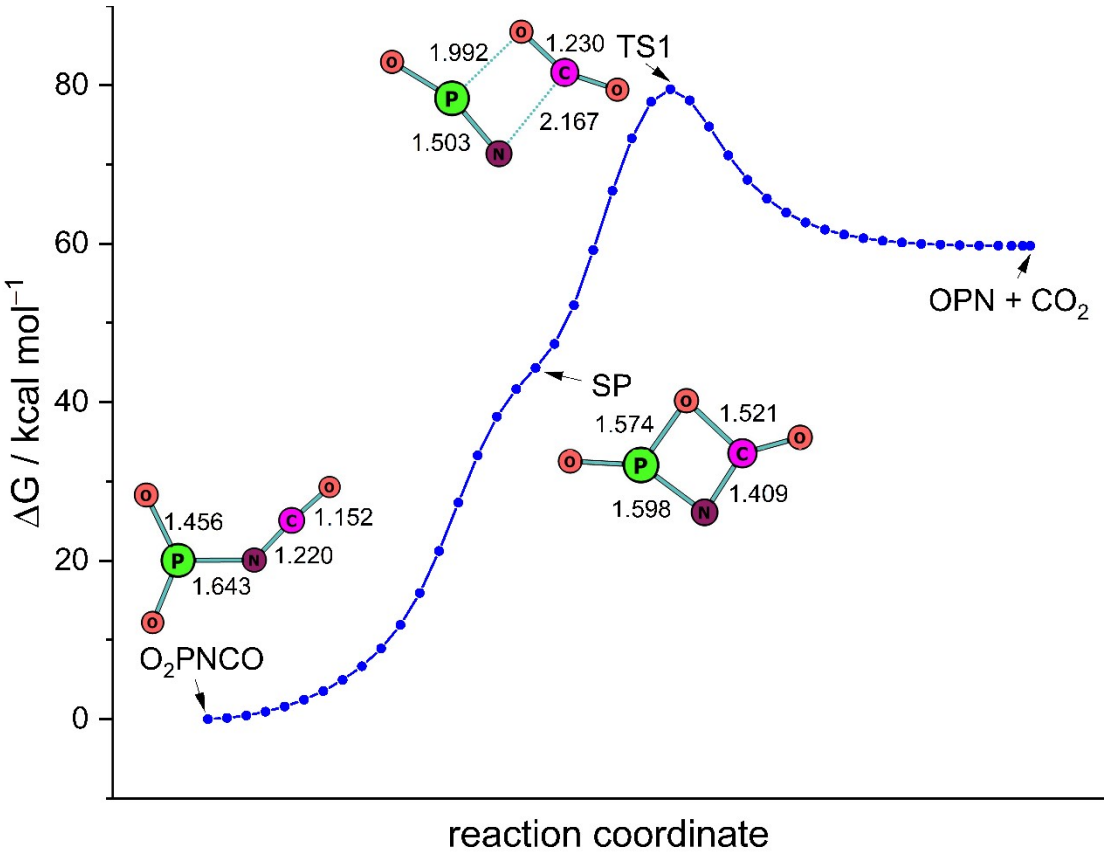

Figure S9. Calculated energy profile along intrinsic reaction coordinate (IRC) for the decomposition of O_2PNCO to OPN/CO_2 via transition state TS1 at the B3LYP/6-311++G(3df, 3pd) level of theory. Bond lengths (Å) calculated at B3LYP/6-311++G(3df, 3pd) level of theory.

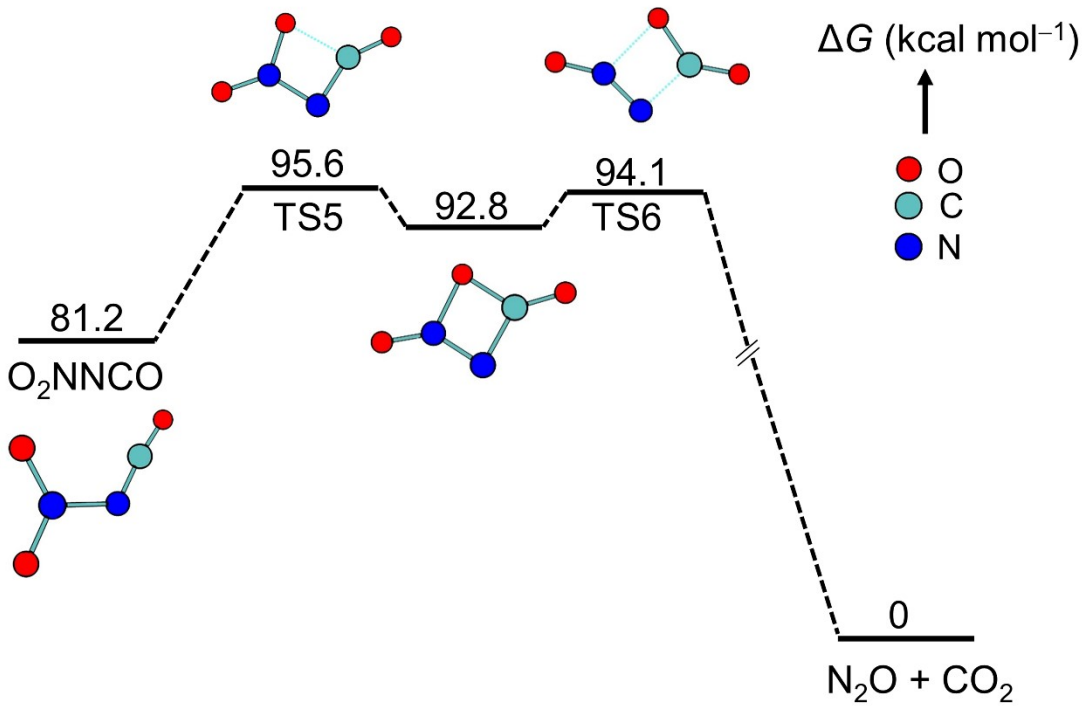

Figure S10. Calculated potential energy profile for the decomposition of O_2NNCO at the B3LYP/6-311++G(3df, 3pd) level of theory.

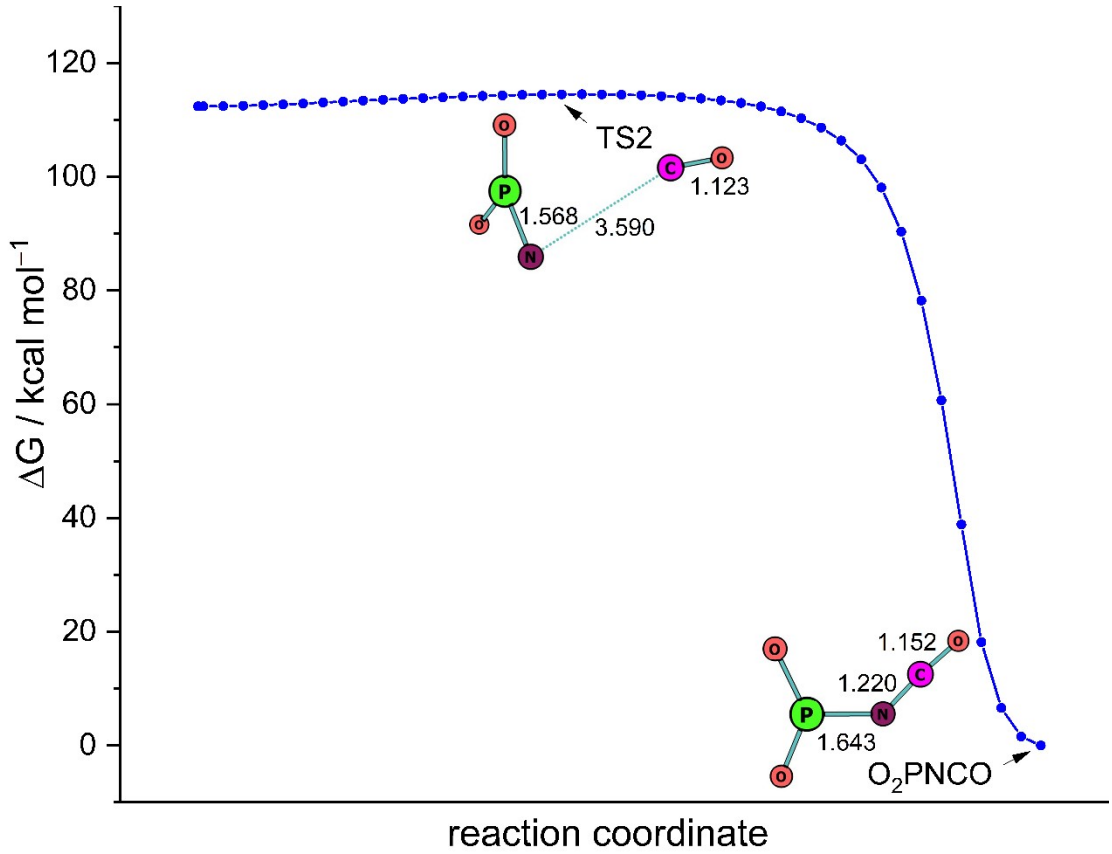

Figure S11. Calculated energy profile along intrinsic reaction coordinate (IRC) for the decomposition of O_2PNCO to O_2PN/CO via transition state TS2 at the B3LYP/6-311++G(3df, 3pd) level of theory. Bond lengths (Å) calculated at B3LYP/6-311++G(3df, 3pd) level of theory.

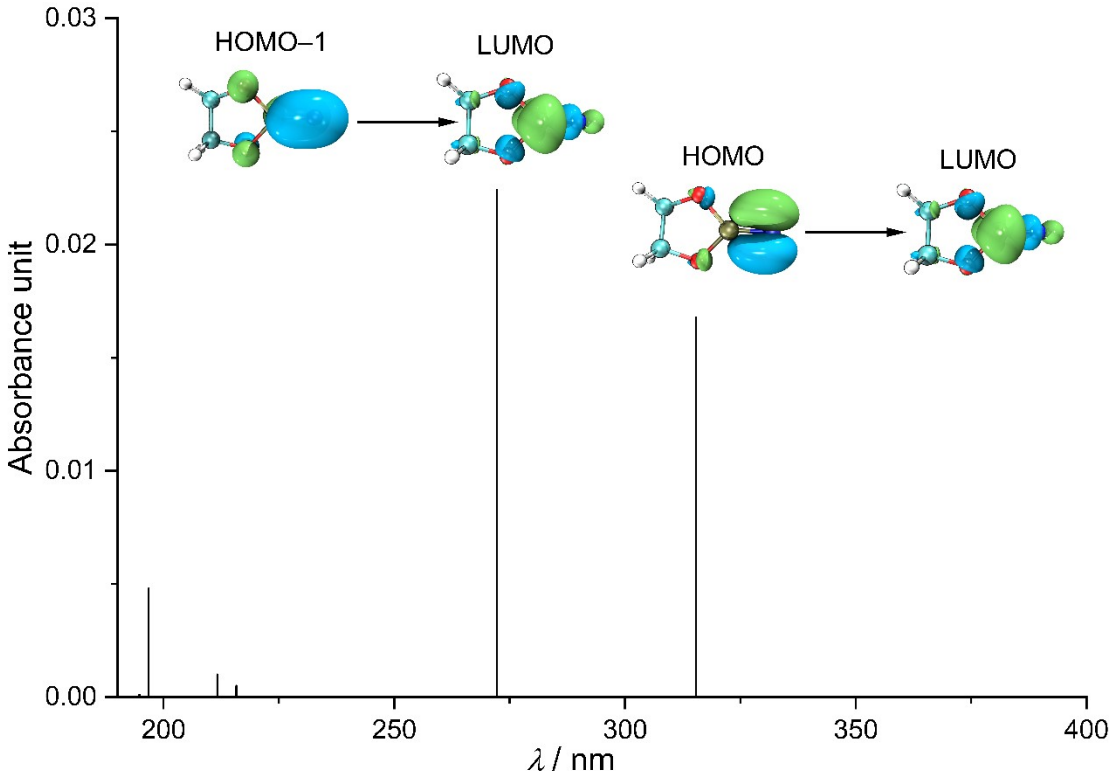

Figure S12. TD-B3LYP/6-311++G(3df, 3pd) calculated vertical transition energies of singlet $C_2H_4O_2PN$. Molecular orbitals for the dominant excitations are depicted.

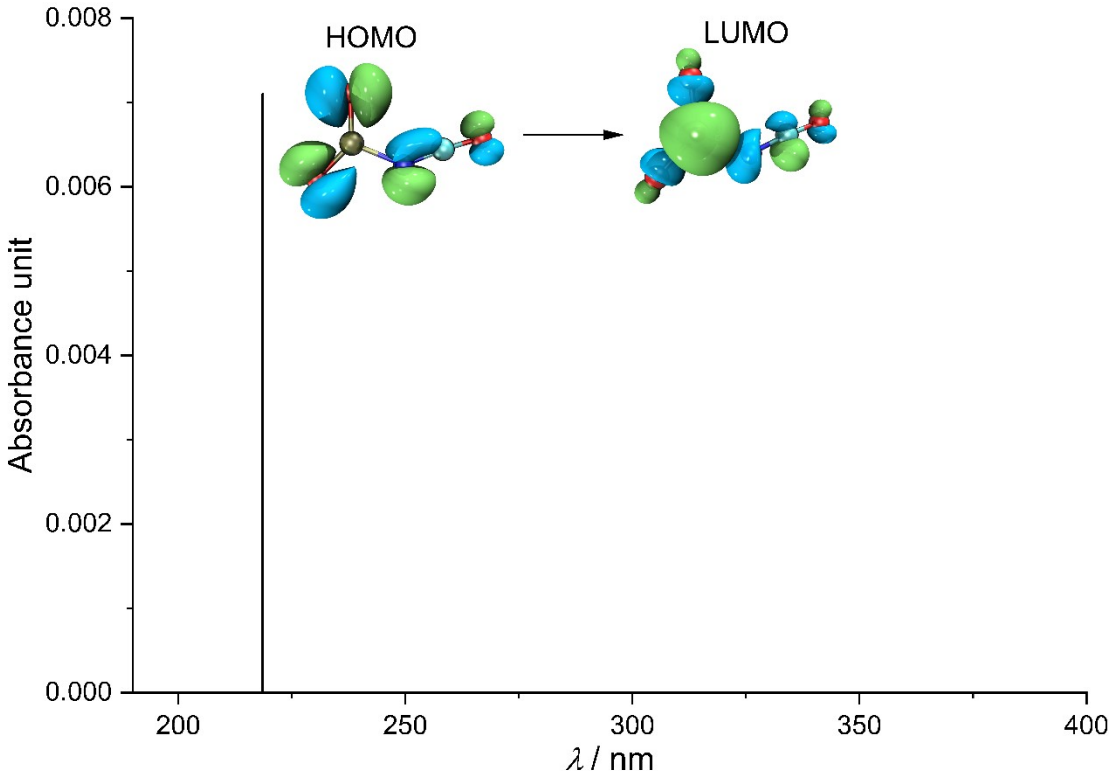

Figure S13. TD-B3LYP/6-311++G(3df, 3pd) calculated vertical transition energies of O_2PNCO. Molecular orbitals for the dominant excitations are depicted.

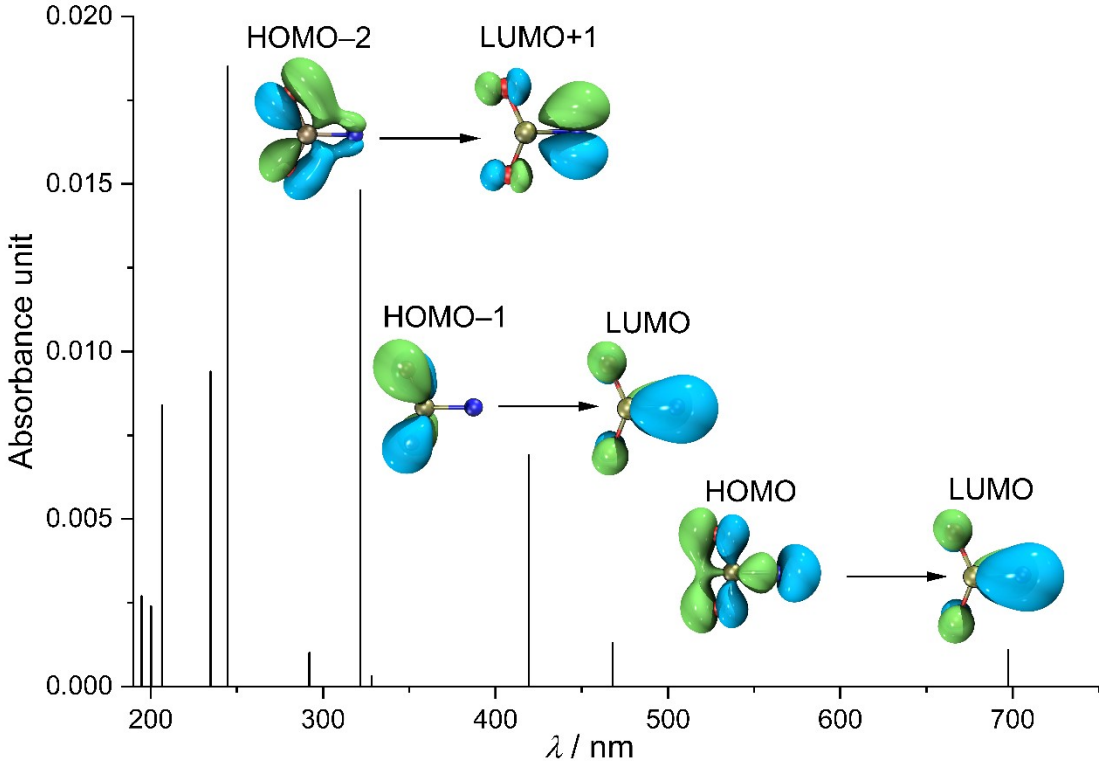

Figure S14. TD-B3LYP/6-311++G(3df, 3pd) calculated vertical transition energies of triplet O_2PN. Molecular orbitals for the dominant excitations are depicted.

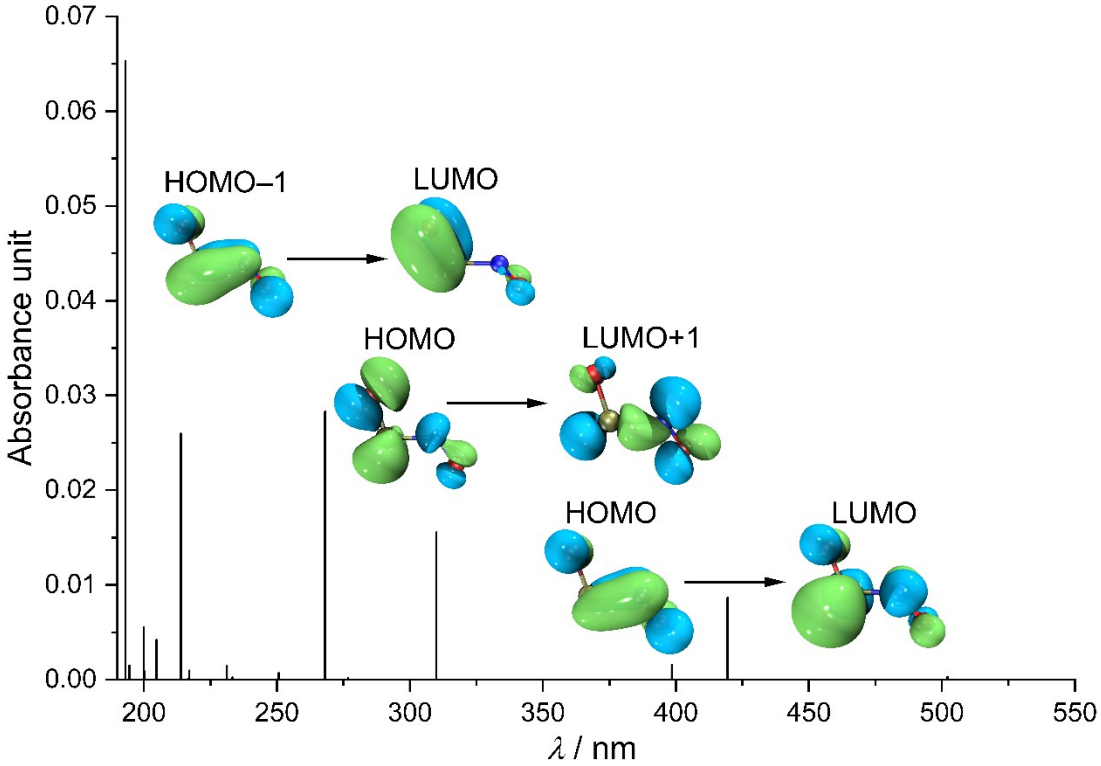

Figure S15. TD-B3LYP/6-311++G(3df, 3pd) calculated vertical transition energies of triplet *trans*-OPNO. Molecular orbitals for the dominant excitations are depicted.

Table S1. Calculated vibrational frequencies (cm^{-1}, unscaled) and intensities (km mol^{-1}, in parentheses) of O_2PNCO.

VPT2[a]	VCI[a]	B3LYP[b]	MPW1PW91[b]	BP86[b]
2277.2	2280.8 (1035)	2354 (1328)	2390 (1324)	2289 (1092)
1451.6	1451.9 (266)	1467 (154)	1488 (177)	1404 (104)
1407.3	1407.8 (116)	1459 (175)	1484 (168)	1399 (161)
1156.9	1157.6 (159)	1164 (141)	1189 (142)	1110 (121)
765.0	765.1 (121)	739 (108)	765 (108)	705 (93)
625.5	622.9 (46)	632 (26)	645 (26)	596 (17)
618.5	616.9 (52)	621 (53)	632 (48)	590 (44)
435.2	435.3 (92)	430 (59)	437 (62)	406 (47)
423.6	423.7 (80)	421 (47)	432 (48)	394 (36)
380.7	381.1 (9)	382 (7)	385 (7)	363 (6)
96.1	96.6 (1)	92 (< 1)	92 (< 1)	90 (< 1)
82.6	81.6 (2)	84 (1)	83 (1)	78 (1)

[a] Anharmonic frequencies obtained with the CCSD(T)-F12/cc-pVTZ-F12 method. Abnormal IR intensities were obtained with the VPT2 method. [b] Harmonic frequencies obtained at the 6-311++G(3df, 3pd) basis set.

Table S2. Calculated IR spectra of O_2PN and OPNO.

triplet O_2PN			singlet O_2PN			triplet *trans*-OPNO			singlet *trans*-OPNO		
B3LYP [a]	VPT2[b]		B3LYP [a]	VPT2[b]		B3LYP [a]	VPT2[b]		B3LYP [a]	VPT2[b]	
ν_{harm}	ν_{harm}	ν_{anharm}	ν_{harm}	ν_{harm}	ν_{anharm}	ν_{harm}	ν_{harm}	ν_{anharm}	ν_{harm}	ν_{harm}	ν_{anharm}
1427 (113)	1451.7 (168)	1431.1	1470 (122)	1469.5 (211)	1448.0	1602 (185)	1575.6 (30)	1572.8	1722 (355)	1660.0 (212)	1622.8
1140 (17)	1152.5 (60)	1134.5	1082 (8)	1065.3 (7)	1048.4	1255 (118)	1263.5 (195)	1246.5	1233 (134)	1242.2 (243)	1226.6
743 (< 1)	755.5 (21)	729.8	995 (6)	982.9 (36)	973.2	547 (52)	611.0 (174)	595.0	581 (18)	574.1 (194)	521.6
418 (44)	424.5 (79)	416.2	384 (35)	371.7 (71)	366.4	375 (4)	390.0 (< 1)	387.4	473 (3)	460.7 (4)	437.0
362 (59)	369.1 (96)	348.7	364 (45)	355.9 (86)	353.7	240 (6)	241.6 (17)	240.1	183 (5)	173.0 (10)	151.2
264 (5)	282.1 (16)	277.1	253 (5)	296.0 (19)	285.5	199 (1)	196.4 (2)	201.9	170 (3)	134.9 (14)	91.6

[a] Calculated vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}, parentheses) at the 6-311++G(3df, 3pd) basis set. [b] Calculated VPT2 IR frequencies (cm^{-1}) and intensities (km mol^{-1}, parentheses) at the CCSD(T)-F12a/cc-pVTZ-F12 level.

Table S3. Calculated and observed IR spectra of $C_2H_4O_2PN$.

B3LYP[a]		MPW1PW91[a]		BP86[a]		Obs.[b]	
singlet	triplet	singlet	triplet	singlet	triplet	Ar-matrix	N_2-matrix
3137 (12)	3128 (15)	3162 (11)	3152 (14)	3058 (13)	3051 (11)	n.o.	n.o.
3123 (11)	3107 (10)	3149 (10)	3132 (10)	3045 (11)	3031 (9)	n.o.	n.o.
3062 (21)	3061 (36)	3084 (20)	3081 (36)	2982 (24)	2980 (29)	n.o.	n.o.
3059 (33)	3055 (16)	3081 (32)	3074 (16)	2977 (34)	2977 (14)	n.o.	n.o.
1522 (< 1)	1518 (1)	1524 (< 1)	1519 (1)	1463 (< 1)	1456 (1)	n.o.	n.o.
1515 (4)	1506 (4)	1515 (5)	1505 (5)	1457 (4)	1443 (5)	1494.2	1500.3
1405 (66)	1374 (< 1)	1434 (89)	1383 (< 1)	1348 (48)	1316 (1)	1370.6	1372.7
1382 (29)	1366 (< 1)	1394 (13)	1369 (< 1)	1328 (32)	1305 (< 1)	1350.7	1350.8
1377 (< 1)	1247 (2)	1379 (< 1)	1255 (2)	1319 (< 1)	1198 (< 1)	n.o.	n.o.
1252 (7)	1234 (2)	1260 (7)	1244 (2)	1207 (5)	1186 (1)	1242.6	n.o.
1243 (3)	1139 (< 1)	1254 (3)	1144 (1)	1198 (2)	1087 (< 1)	1230.2	1230.0
1143 (4)	1007 (148)	1149 (14)	1053 (176)	1098 (4)	961 (15)	1126.1	n.o.
1044 (234)	1003 (6)	1088 (241)	1041 (5)	999 (165)	959 (55)	1036.8	1040.3
1034 (15)	918 (66)	1072 (15)	943 (47)	990 (11)	880 (56)	n.o.	1032.9
929 (63)	854 (2)	951 (49)	864 (3)	898 (67)	822 (2)	924.0	n.o.
873 (7)	773 (49)	887 (12)	802 (53)	846 (7)	730 (16)	867.0	n.o.
784 (131)	732 (100)	809 (127)	758 (100)	740 (115)	707 (29)	799.2	805.5
754 (31)	688 (1)	779 (32)	696 (1)	705 (36)	694 (79)	763.7	769.7
636 (< 1)	643 (< 1)	641 (< 1)	649 (< 1)	603 (1)	614 (2)	n.o.	n.o.
547 (13)	526 (32)	553 (13)	533 (33)	521 (14)	498 (27)	545.5	547.4
310 (14)	328 (11)	322 (15)	334 (11)	299 (11)	318 (7)	n.o.	n.o.
287 (6)	246 (14)	295 (7)	256 (13)	273 (4)	196 (11)	n.o.	n.o.
178 (< 1)	160 (9)	183 (< 1)	168 (8)	184 (< 1)	151 (9)	n.o.	n.o.
136 (< 1)	90 (2)	138 (< 1)	94 (2)	134 (< 1)	89 (2)	n.o.	n.o.

[a] Calculated harmonic vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}, in parentheses) at the 6-311++G(3df, 3pd) basis set. [b] Observed band positions (> 400 cm^{-1}) for the most intense matrix sites.

Table S4. Calculated vertical excitation energies and oscillator strength of O_2PNCO and O_2PN at TD-DFT B3LYP/6-311++G(3df, 3pd) level of theory.

O_2PNCO		triplet O_2PN		singlet O_2PN	
λ/nm	oscillator strength	λ/nm	oscillator strength	λ/nm	oscillator strength
237.43	0.0000	697.38	0.0011	854.70	0.0002
236.08	0.0000	467.99	0.0000	601.60	0.0000
229.22	0.0000	467.91	0.0013	527.11	0.0000
222.92	0.0000	419.31	0.0069	357.01	0.0024
218.61	0.0071	328.11	0.0003	332.32	0.0000
213.98	0.0000	321.59	0.0148	297.07	0.0002
210.48	0.0000	292.12	0.0010	278.40	0.0000
202.44	0.0000	244.69	0.0185	262.35	0.0000
199.82	0.0000	242.95	0.0000	253.14	0.0033
199.52	0.0000	234.75	0.0094	247.62	0.0101
195.27	0.0000	218.41	0.0000	240.61	0.0000
190.73	0.0000	210.07	0.0000	213.87	0.0180
		206.65	0.0084	213.24	0.0000
		202.23	0.0000	210.27	0.0000
		200.27	0.0024	210.04	0.0000
		198.87	0.0000	200.95	0.0000
		194.76	0.0027	197.07	0.0020
				193.80	0.0000
				193.04	0.0029

Table S5. Calculated vertical excitation energies and oscillator strength of OPNO at TD-DFT B3LYP/6-311++G(3df, 3pd) level of theory.

singlet *cis*-OPNO		triplet *cis*-OPNO		singlet *trans*-OPNO		triplet *trans*-OPNO	
λ/nm	oscillator strength	λ/nm	oscillator strength	λ/nm	oscillator strength	λ/nm	oscillator strength
10155.26	0.0000	466.07	0.0000	2811.24	0.0001	502.04	0.0005
1021.90	0.0000	404.37	0.0024	642.98	0.0000	419.48	0.0144
657.66	0.0004	398.23	0.0156	495.99	0.0000	398.46	0.0026
420.70	0.0000	312.30	0.0411	422.03	0.0057	309.93	0.0259
364.57	0.0000	285.25	0.0000	302.57	0.0000	276.73	0.0003
320.01	0.0000	275.04	0.0294	286.37	0.0000	268.09	0.0472
296.46	0.0019	252.78	0.0024	281.10	0.0100	250.63	0.0012
287.58	0.0000	235.90	0.0002	279.23	0.0000	233.23	0.0004
279.71	0.0000	234.39	0.0039	269.05	0.0029	231.19	0.0024
271.56	0.0391	223.83	0.0009	233.72	0.0000	217.04	0.0016
241.50	0.0050	216.57	0.0178	230.08	0.0127	216.73	0.0002
239.51	0.1418	209.71	0.0034	216.35	0.0005	213.85	0.0433
232.94	0.0000	205.18	0.0033	212.84	0.0000	204.67	0.0070
232.23	0.0000	203.89	0.0051	212.07	0.3242	200.11	0.0015
231.53	0.0000	198.83	0.0030	205.66	0.0000	199.99	0.0092
221.12	0.1549	192.14	0.0538	203.22	0.0000	194.55	0.0025
205.95	0.0000	190.54	0.0096	197.30	0.0094	193.05	0.1088
205.01	0.0026			194.18	0.0000		
201.82	0.0644						
198.02	0.0177						
197.60	0.0000						
194.36	0.0000						

Table S6. Calculated vertical excitation energies and oscillator strength of $C_2H_4O_2PNCO$, $C_2H_4O_2PN_3$ and $C_2H_4O_2PN$ at TD-DFT B3LYP/6-311++G(3df, 3pd) level of theory.

$C_2H_4O_2PNCO$		$C_2H_4O_2PN_3$		triplet $C_2H_4O_2PN$		singlet $C_2H_4O_2PN$	
λ/nm	oscillator strength	λ/nm	oscillator strength	λ/nm	oscillator strength	λ/nm	oscillator strength
257.48	0.0000	293.13	0.0000	1027.19	0.0005	366.12	0.0000
237.44	0.0000	276.09	0.0000	709.77	0.0047	339.93	0.0000
206.03	0.0375	263.88	0.0000	341.59	0.0143	315.33	0.0168
205.73	0.0000	262.15	0.0000	321.06	0.0013	310.70	0.0000
202.35	0.0000	244.98	0.0002	316.98	0.0002	292.37	0.0000
199.79	0.0292	234.76	0.0170	274.62	0.0302	272.26	0.0224
199.02	0.0000	229.46	0.0162	257.02	0.0030	258.96	0.0000
193.22	0.0125	223.63	0.0000	246.74	0.0020	235.26	0.0000
190.08	0.0239	211.43	0.0000	241.19	0.0036	215.81	0.0005
		201.66	0.0000	234.22	0.0089	212.38	0.0000
		199.25	0.0800	229.54	0.0021	211.67	0.0010
		195.84	0.0000	224.97	0.0014	207.78	0.0000
		194.26	0.0000	216.13	0.0010	204.26	0.0000
		193.02	0.1315	200.21	0.0053	197.35	0.0000
		190.47	0.1303	197.46	0.0124	196.79	0.0048
				196.48	0.0140	194.78	0.0001
				191.20	0.0407		

Table S7. Calculated vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}, parentheses) of O_2PNCO isomers at the B3LYP/6-311++G(3df, 3pd) level of theory.

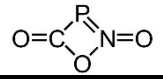	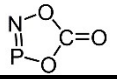	O_2PCNO	O_2POCN	O_2NCPO	O_2NOCP	O_2NPCO	OPC(O)NO
1904 (305)	1904 (646)	2377 (1148)	2380 (122)	1557 (376)	1874 (340)	2109 (641)	1876 (212)
1668 (828)	1102 (74)	1477 (30)	1493 (150)	1330 (183)	1687 (121)	1562 (280)	1633 (52)
1092 (94)	1025 (82)	1465 (152)	1178 (237)	1266 (137)	1345 (717)	1328 (330)	1231 (88)
756 (11)	960 (178)	1154 (171)	1133 (96)	1177 (37)	876 (7)	835 (67)	949 (21)
709 (12)	852 (10)	596 (196)	733 (103)	750 (12)	743 (356)	675 (21)	595 (10)
616 (16)	777 (11)	572 (4)	555 (34)	741 (9)	571 (4)	619 (2)	562 (26)
615 (4)	765 (21)	537 (5)	501 (11)	555 (2)	493 (< 1)	513 (8)	428 (1)
580 (1)	711 (< 1)	407 (45)	404 (40)	316 (8)	454 (8)	463 (< 1)	296 (38)
489 (49)	609 (27)	382 (26)	403 (42)	278 (3)	312 (1)	356 (2)	175 (5)
409 (14)	473 (8)	371 (3)	366 (3)	206 (11)	187 (3)	296 (< 1)	161 (11)
313 (8)	438 (10)	94 (4)	136 (4)	105 (2)	88 (< 1)	130 (1)	103 (2)
172 (2)	192 (< 1)	68 (2)	99 (6)	98 (6)	82 (1)	68 (< 1)	54 (6)

Table S8. Calculated vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}, parentheses) of O_2PN isomers at the B3LYP/6-311++G(3df, 3pd) level of theory.

cyclic-$O_2P(\equiv N)$	triplet O_2NP	singlet O_2NP	*cyclic*-$O_2N(\equiv P)$	*cyclic*-OOPN	$(P{=}N)(O)_2$
1449 (34)	1528 (313)	1422 (248)	1269 (401)	1045 (< 1)	1065 (20)
945 (37)	1337 (144)	1290 (213)	957 (2)	971 (62)	840 (97)
787 (12)	828 (20)	834 (2)	626 (46)	914 (< 1)	824 (16)
533 (22)	550 (7)	639 (< 1)	398 (< 1)	755 (29)	679 (14)
273 (15)	407 (9)	480 (1)	351 (4)	616 (14)	476 (13)
246 (17)	226 (< 1)	293*i*	261*i*	490 (9)	211 (2)
singlet *cis*-OPNO	triplet *cis*-OPNO	triplet *cis*-OPON	triplet *trans*-OPON	triplet *cyclic*-OPN(═O)	
1695 (340)	1620 (152)	1293 (104)	1301 (119)	1210 (54)	
1259 (99)	1243 (105)	1076 (44)	1117 (74)	1004 (32)	
573 (22)	489 (76)	564 (153)	605 (171)	669 (13)	
288 (1)	414 (3)	459 (13)	372 (5)	548 (10)	
191 (2)	237 (4)	223 (4)	229 (10)	317 (15)	
66 (5)	197 (3)	196 (2)	155 (3)	250 (8)	

Table S9. Calculated relative energies (kcal mol^{-1}) of OPNO.

	B3LYP[a]	CBS-QB3	CCSD(T)[b]
singlet *cis*-OPNO	15	10	7
triplet *cis*-OPNO	0.3	0.5	0.6
singlet *trans*-OPNO	13	8	6
triplet *trans*-OPNO	0	0	0

[a] At the B3LYP/6-311++G(3df, 3pd) level. [b] At the CCSD(T)-F12a/aug-cc-pVTZ level.

Table S10. Calculated vertical excitation energies and oscillator strength of HNCO isomers at TD-DFT B3LYP/6-311++G(3df, 3pd) level of theory.

HNCO		HOCN		HCNO	
λ/nm	oscillator strength	λ/nm	oscillator strength	λ/nm	oscillator strength
203.80	0.0000	202.94	0.0000	275.92	0.0000
198.29	0.0000	195.32	0.0000	246.35	0.0000
		194.44	0.0018	246.35	0.0000
				216.18	0.0000
				216.18	0.0000
				209.03	0.0000
				209.03	0.0000

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Calculated atomic coordinates (in Angstroms) and energies (in Hartrees) of all optimized structures.

O_2PNCO
B3LYP/6-311++G(3df, 3pd)

P	-0.92183400	0.04884600	0.00000000
O	-0.92391100	1.50398500	0.00000000
O	-1.97327300	-0.95125200	-0.00000100
N	0.57300800	-0.62777200	0.00000100
C	1.71887900	-0.21625600	0.00000100
O	2.83508100	0.06717200	-0.00000100

Zero-point correction= 0.022441 (Hartree/Particle)
Thermal correction to Energy= 0.028105
Thermal correction to Enthalpy= 0.029049
Thermal correction to Gibbs Free Energy= -0.008065
Sum of electronic and zero-point Energies= -660.070057
Sum of electronic and Thermal Energies= -660.064393
Sum of electronic and Thermal Enthalpies= -660.063449
Sum of electronic and Thermal Free Energies= -660.100563

CCSD(T)-F12A/VTZ-F12 ENERGY=-659.24037289

P	0.0000000000	-0.0565429039	-0.8923706522
O	0.0000000000	-1.5058404942	-0.7806086369
O	0.0000000000	0.8589758502	-2.0151748213
N	0.0000000000	0.7335903339	0.5481573044
C	0.0000000000	0.2559756414	1.6800893038
O	0.0000000000	-0.0779208133	2.7834743961

singlet O_2PN
B3LYP/6-311++G(3df, 3pd)

P	-0.15174100	0.04378300	-0.00011800
N	1.07397600	1.02290400	0.00007400
O	0.94229300	-0.98817700	0.00005800
O	-1.59750700	0.01104400	0.00009900

Zero-point correction= 0.010367 (Hartree/Particle)
Thermal correction to Energy= 0.014421
Thermal correction to Enthalpy= 0.015366
Thermal correction to Gibbs Free Energy= -0.016363
Sum of electronic and zero-point Energies= -546.541840
Sum of electronic and Thermal Energies= -546.537785
Sum of electronic and Thermal Enthalpies= -546.536841
Sum of electronic and Thermal Free Energies= -546.568570

CCSD(T)-F12A/VTZ-F12 ENERGY=-545.86242934

P	0.0578213161	0.0000000000	-0.1519183145
N	1.0063381473	0.0000000000	1.0954582067
O	-1.0019879067	0.0000000000	0.9318878240
O	0.0089990691	0.0000000000	-1.5967428647

triplet O_2PN
B3LYP/6-311++G(3df, 3pd)

P	0.00000000	0.00000000	0.07592800
N	0.00000000	0.00000000	-1.62459200
O	0.00000000	1.34366900	0.63957700
O	0.00000000	-1.34366900	0.63957700

Zero-point correction= 0.009925 (Hartree/Particle)
Thermal correction to Energy= 0.013988
Thermal correction to Enthalpy= 0.014932
Thermal correction to Gibbs Free Energy= -0.017321
Sum of electronic and zero-point Energies= -546.567427
Sum of electronic and Thermal Energies= -546.563364
Sum of electronic and Thermal Enthalpies= -546.562420
Sum of electronic and Thermal Free Energies= -546.594673

UCCSD(T)-F12A/VTZ-F12 ENERGY=-545.87781275
P 0.0000000000 0.0000000000 0.0809328977
N 0.0000000000 -0.0000000001 -1.6310764414
O 0.0000000000 1.3439771652 0.6356172505
O 0.0000000000 -1.3439771651 0.6356172507

singlet *trans*-OPNO
B3LYP/6-311++G(3df, 3pd)
P 0.00000000 0.76574000 0.00000000
O 1.43335700 1.11139100 0.00000000
N -0.37915100 -0.86161100 0.00000000
O -1.10160000 -1.79324400 0.00000000
Zero-point correction= 0.009946 (Hartree/Particle)
Thermal correction to Energy= 0.014405
Thermal correction to Enthalpy= 0.015349
Thermal correction to Gibbs Free Energy= -0.017365
Sum of electronic and zero-point Energies= -546.553080
Sum of electronic and Thermal Energies= -546.548621
Sum of electronic and Thermal Enthalpies= -546.547677
Sum of electronic and Thermal Free Energies= -546.580391

CCSD(T)-F12A/VTZ-F12 ENERGY=-545.85750647
P 0.0000000000 -0.4326839085 0.6229131066
O 0.0000000000 0.5445634938 1.7238193632
N 0.0000000000 0.1963981005 -0.9311367338
O 0.0000000000 0.1213778079 -2.1148930362

triplet *trans*-OPNO
B3LYP/6-311++G(3df, 3pd)
P 0.00000000 0.77951600 0.00000000
O 1.44562400 1.03369700 0.00000000
N -0.22150100 -1.00452200 0.00000000
O -1.25181100 -1.61633300 0.00000000
Zero-point correction= 0.009614 (Hartree/Particle)
Thermal correction to Energy= 0.014051
Thermal correction to Enthalpy= 0.014995
Thermal correction to Gibbs Free Energy= -0.018642
Sum of electronic and zero-point Energies= -546.573237
Sum of electronic and Thermal Energies= -546.568800
Sum of electronic and Thermal Enthalpies= -546.567856
Sum of electronic and Thermal Free Energies= -546.601493

UCCSD(T)-F12A/VTZ-F12 ENERGY=-545.86849525
P 0.0000000000 -0.4629771050 0.5983667590
O 0.0000000000 0.5170248466 1.6886958200

N 0.0000000000 0.4474695551 -0.9229730209
O 0.0000000000 -0.0122271182 -2.0393831678

singlet *cis*-OPNO
B3LYP/6-311++G(3df, 3pd)
P 0.00000000 0.99077000 0.00000000
O 1.37951700 0.48156600 0.00000000
N -1.12492300 -0.75530900 0.00000000
O -0.39520900 -1.67836400 0.00000000
Zero-point correction= 0.009280 (Hartree/Particle)
Thermal correction to Energy= 0.014113
Thermal correction to Enthalpy= 0.015058
Thermal correction to Gibbs Free Energy= -0.019138
Sum of electronic and zero-point Energies= -546.548466
Sum of electronic and Thermal Energies= -546.543632
Sum of electronic and Thermal Enthalpies= -546.542688
Sum of electronic and Thermal Free Energies= -546.576883

triplet *cis*-OPNO
B3LYP/6-311++G(3df, 3pd)
P 0.76782200 -0.49964400 -0.00024700
O 1.27113100 0.88216700 0.00024500
N -1.05066800 -0.46914700 0.00067100
O -1.79146200 0.46516900 -0.00036900
Zero-point correction= 0.009575 (Hartree/Particle)
Thermal correction to Energy= 0.014021
Thermal correction to Enthalpy= 0.014966
Thermal correction to Gibbs Free Energy= -0.018850
Sum of electronic and zero-point Energies= -546.572432
Sum of electronic and Thermal Energies= -546.567986
Sum of electronic and Thermal Enthalpies= -546.567042
Sum of electronic and Thermal Free Energies= -546.600857

TS1
B3LYP/6-311++G(3df, 3pd)
O 2.19995000 -0.48878400 -0.00057600
P 0.95597300 0.26584600 0.00017200
N -0.01782500 1.41139200 0.00023000
O -0.47818700 -1.11791400 0.00054700
C -1.37595900 -0.27674100 0.00000300
O -2.46664500 0.08082400 -0.00049800
Zero-point correction= 0.019610 (Hartree/Particle)
Thermal correction to Energy= 0.025130
Thermal correction to Enthalpy= 0.026075
Thermal correction to Gibbs Free Energy= -0.010166
Sum of electronic and zero-point Energies= -659.946132
Sum of electronic and Thermal Energies= -659.940612
Sum of electronic and Thermal Enthalpies= -659.939668
Sum of electronic and Thermal Free Energies= -659.975908

TS2
B3LYP/6-311++G(3df, 3pd)
O 0.62893100 0.15858400 0.64772800
N 0.73521300 1.35667500 3.24490900

C 2.35828600 -1.84628700 3.21876900
O 3.02271600 -2.67709300 3.58019300
P 0.21967900 0.83349500 1.85937700
O -1.06730200 1.43336000 2.35846100
Zero-point correction= 0.015880 (Hartree/Particle)
Thermal correction to Energy= 0.023290
Thermal correction to Enthalpy= 0.024234
Thermal correction to Gibbs Free Energy= -0.019875
Sum of electronic and zero-point Energies= -659.894003
Sum of electronic and Thermal Energies= -659.886593
Sum of electronic and Thermal Enthalpies= -659.885649
Sum of electronic and Thermal Free Energies= -659.929758

TS3
B3LYP/6-311++G(3df, 3pd)
P 0.27542500 0.11229400 0.29692900
N -1.12401100 0.73391200 -0.22874700
O 1.60523000 -0.11179800 -0.28583900
O -1.13814200 -0.74092600 -0.07074900
Zero-point correction= 0.008545 (Hartree/Particle)
Thermal correction to Energy= 0.012267
Thermal correction to Enthalpy= 0.013212
Thermal correction to Gibbs Free Energy= -0.017886
Sum of electronic and zero-point Energies= -546.492774
Sum of electronic and Thermal Energies= -546.489052
Sum of electronic and Thermal Enthalpies= -546.488108
Sum of electronic and Thermal Free Energies= -546.519205

$C_2H_4O_2PNCO$
B3LYP/6-311++G(3df, 3pd)
C -1.76699300 -0.89877400 0.67045300
H -2.69646500 -1.46109200 0.63477800
H -1.14388000 -1.27041900 1.48382000
C -1.99576000 0.61844000 0.77402400
H -2.98917100 0.90845100 0.43468700
H -1.83416900 0.98636500 1.78545400
O -1.08069900 -1.10475600 -0.57879400
O -1.03925200 1.24004200 -0.10885300
P -0.12334900 0.16794900 -0.93046200
N 1.13900000 -0.09368300 0.23740500
O 3.50289000 -0.01886300 0.38936900
C 2.34232100 -0.04602400 0.27928800
Zero-point correction= 0.079944 (Hartree/Particle)
Thermal correction to Energy= 0.087660
Thermal correction to Enthalpy= 0.088604
Thermal correction to Gibbs Free Energy= 0.045888
Sum of electronic and zero-point Energies= -738.655874
Sum of electronic and Thermal Energies= -738.648159
Sum of electronic and Thermal Enthalpies= -738.647215
Sum of electronic and Thermal Free Energies= -738.689931

$C_2H_4O_2PN_3$
B3LYP/6-311++G(3df, 3pd)
C -1.82740300 -0.89294100 0.56367200

H	-2.73747200	-1.46962500	0.42002300
H	-1.30866600	-1.23911900	1.45752800
C	-2.08382500	0.62048400	0.60182100
H	-3.01221200	0.89261500	0.10090500
H	-2.09003400	1.00877100	1.61832000
O	-0.98234300	-1.11071000	-0.58264300
O	-1.00058400	1.23562000	-0.12447600
P	0.00582100	0.16309700	-0.83070700
N	1.12510300	-0.08586500	0.52069200
N	2.33207300	-0.04258200	0.32724700
N	3.45594400	-0.01492900	0.22746400

Zero-point correction= 0.079526 (Hartree/Particle)
Thermal correction to Energy= 0.087248
Thermal correction to Enthalpy= 0.088193
Thermal correction to Gibbs Free Energy= 0.045408
Sum of electronic and zero-point Energies= -734.751626
Sum of electronic and Thermal Energies= -734.743904
Sum of electronic and Thermal Enthalpies= -734.742960
Sum of electronic and Thermal Free Energies= -734.785744

singlet $C_2H_4O_2PN$

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

C	1.54668500	0.75427300	0.13902300
H	2.21317100	1.30196700	-0.52182600
H	1.78967300	0.97893000	1.17749300
C	1.54680800	-0.75408300	-0.13894700
H	1.78986500	-0.97858500	-1.17744200
H	2.21333700	-1.30176500	0.52186100
O	0.20028300	1.19623500	-0.11513300
O	0.20046300	-1.19630000	0.11516700
P	-0.88161000	-0.00012500	-0.00012600
N	-2.36411800	0.00010200	0.00015300

Zero-point correction= 0.070040 (Hartree/Particle)
Thermal correction to Energy= 0.075738
Thermal correction to Enthalpy= 0.076682
Thermal correction to Gibbs Free Energy= 0.040394
Sum of electronic and zero-point Energies= -625.189175
Sum of electronic and Thermal Energies= -625.183477
Sum of electronic and Thermal Enthalpies= -625.182533
Sum of electronic and Thermal Free Energies= -625.218820

triplet $C_2H_4O_2PN$

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

C	1.24989800	0.84090900	0.32821100
H	2.10669300	1.39454000	-0.04758500
H	1.02947100	1.15205200	1.34943500
C	1.44454600	-0.68376800	0.22947800
H	2.19625900	-0.95100900	-0.51180000
H	1.70637600	-1.12106300	1.19116600
O	0.12392300	1.15773200	-0.51460100
O	0.19219300	-1.24515900	-0.21792200
P	-0.94566800	-0.08708800	-0.46607800
N	-1.64990900	0.08405300	1.07485700

Zero-point correction= 0.067697 (Hartree/Particle)

Thermal correction to Energy= 0.073694
Thermal correction to Enthalpy= 0.074638
Thermal correction to Gibbs Free Energy= 0.036573
Sum of electronic and zero-point Energies= -625.153145
Sum of electronic and Thermal Energies= -625.147149
Sum of electronic and Thermal Enthalpies= -625.146205
Sum of electronic and Thermal Free Energies= -625.184269

(O=)PCON(=O)

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

C	-1.08905900	-0.17040200	0.00000300
O	-0.11243100	-1.17421700	0.00021700
O	2.11755500	-0.56585600	-0.00014300
O	-2.25189700	-0.37324400	-0.00015000
P	0.09744700	1.27261200	0.00004800
N	1.00669000	-0.16574800	-0.00001900

Zero-point correction= 0.021256 (Hartree/Particle)
Thermal correction to Energy= 0.026332
Thermal correction to Enthalpy= 0.027277
Thermal correction to Gibbs Free Energy= -0.007799
Sum of electronic and zero-point Energies= -659.880815
Sum of electronic and Thermal Energies= -659.875739
Sum of electronic and Thermal Enthalpies= -659.874795
Sum of electronic and Thermal Free Energies= -659.909871

***cyclic*-ONPOC(=O)**

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

P	1.44107100	-0.40883400	0.00058700
N	0.94661000	1.10717200	-0.00024100
O	-0.44509000	1.16014600	-0.00036100
O	-0.08486600	-1.05428700	-0.00122500
C	-1.04662700	-0.07754300	-0.00012400
O	-2.21536600	-0.24991300	0.00078900

Zero-point correction= 0.022362 (Hartree/Particle)
Thermal correction to Energy= 0.026889
Thermal correction to Enthalpy= 0.027833
Thermal correction to Gibbs Free Energy= -0.006134
Sum of electronic and zero-point Energies= -659.970200
Sum of electronic and Thermal Energies= -659.965673
Sum of electronic and Thermal Enthalpies= -659.964729
Sum of electronic and Thermal Free Energies= -659.998696

O_2PCNO

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

P	-0.00006900	-1.03826900	0.00000000
O	-1.33979100	-1.60121000	0.00000000
O	1.33960800	-1.60132000	0.00000000
C	0.00000000	0.67888200	0.00000000
N	0.00008100	1.84452800	0.00000000
O	0.00024200	3.02616200	0.00000000

Zero-point correction= 0.021660 (Hartree/Particle)
Thermal correction to Energy= 0.027567
Thermal correction to Enthalpy= 0.028511
Thermal correction to Gibbs Free Energy= -0.009249

Sum of electronic and zero-point Energies= -659.954008
Sum of electronic and Thermal Energies= -659.948101
Sum of electronic and Thermal Enthalpies= -659.947157
Sum of electronic and Thermal Free Energies= -659.984917

O_2POCN

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

P	0.85873300	0.09492100	0.00000000
O	0.62006100	1.52313300	0.00000000
O	1.99627000	-0.79787800	0.00000000
C	-1.70331900	-0.27326800	0.00000000
O	-0.50756800	-0.78941200	0.00000000
N	-2.79017000	0.10414900	0.00000000

Zero-point correction= 0.021383 (Hartree/Particle)
Thermal correction to Energy= 0.027126
Thermal correction to Enthalpy= 0.028070
Thermal correction to Gibbs Free Energy= -0.008746
Sum of electronic and zero-point Energies= -660.013987
Sum of electronic and Thermal Energies= -660.008244
Sum of electronic and Thermal Enthalpies= -660.007300
Sum of electronic and Thermal Free Energies= -660.044116

O_2NCPO

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

O	-1.60616100	1.70610100	0.00000000
O	-2.15918500	-0.41890100	0.00000000
C	0.00000000	0.36092500	0.00000000
O	2.67095200	-0.55582600	0.00000000
N	-1.35361600	0.48811400	0.00000000
P	1.21536500	-0.76222200	0.00000000

Zero-point correction= 0.019101 (Hartree/Particle)
Thermal correction to Energy= 0.025217
Thermal correction to Enthalpy= 0.026161
Thermal correction to Gibbs Free Energy= -0.011784
Sum of electronic and zero-point Energies= -659.789842
Sum of electronic and Thermal Energies= -659.783726
Sum of electronic and Thermal Enthalpies= -659.782782
Sum of electronic and Thermal Free Energies= -659.820727

O_2NOCP

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

O	1.06219200	1.26471400	0.00000200
O	2.58500100	-0.31718600	-0.00000200
C	-0.96097200	-0.56641600	0.00000300
O	0.10556300	-1.14057000	0.00000100
N	1.52402500	0.18609000	0.00000000
P	-2.32829300	0.24268000	-0.00000100

Zero-point correction= 0.019868 (Hartree/Particle)
Thermal correction to Energy= 0.026042
Thermal correction to Enthalpy= 0.026986
Thermal correction to Gibbs Free Energy= -0.011332
Sum of electronic and zero-point Energies= -659.817690
Sum of electronic and Thermal Energies= -659.811515
Sum of electronic and Thermal Enthalpies= -659.810571

Sum of electronic and Thermal Free Energies= -659.848889

O_2NPCO

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

O	0.69540700	1.44403100	0.00000000
O	2.21030100	-0.10626100	0.00000000
C	-1.48193900	-0.05366700	0.00000000
N	1.05631700	0.28139000	0.00000000
P	-0.15419100	-1.13440500	0.00000000
O	-2.42942400	0.58327300	0.00000000

Zero-point correction= 0.020413 (Hartree/Particle)
Thermal correction to Energy= 0.026320
Thermal correction to Enthalpy= 0.027264
Thermal correction to Gibbs Free Energy= -0.010231
Sum of electronic and zero-point Energies= -659.883863
Sum of electronic and Thermal Energies= -659.877955
Sum of electronic and Thermal Enthalpies= -659.877011
Sum of electronic and Thermal Free Energies= -659.914506

(OP)C(O)(NO)

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

C	-0.67119000	-0.62946400	-0.02304100
O	-1.06471700	-1.73918100	0.04398900
P	1.13557800	0.03074800	-0.51893200
N	-1.61047200	0.59248200	0.25122300
O	1.82904100	0.07292900	0.78533800
O	-0.98097700	1.56227600	-0.05886900

Zero-point correction= 0.018385 (Hartree/Particle)
Thermal correction to Energy= 0.025109
Thermal correction to Enthalpy= 0.026053
Thermal correction to Gibbs Free Energy= -0.013531
Sum of electronic and zero-point Energies= -659.888129
Sum of electronic and Thermal Energies= -659.881405
Sum of electronic and Thermal Enthalpies= -659.880460
Sum of electronic and Thermal Free Energies= -659.920045

***cyclic*-$O_2P(\equiv N)$**

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

P	0.00000000	0.00000000	0.30355500
O	0.00000000	-0.81108400	-1.06495000
O	0.00000000	0.81108400	-1.06495000
N	0.00000000	0.00000000	1.78369800

Zero-point correction= 0.009650 (Hartree/Particle)
Thermal correction to Energy= 0.013762
Thermal correction to Enthalpy= 0.014706
Thermal correction to Gibbs Free Energy= -0.016398
Sum of electronic and zero-point Energies= -546.467925
Sum of electronic and Thermal Energies= -546.463812
Sum of electronic and Thermal Enthalpies= -546.462868
Sum of electronic and Thermal Free Energies= -546.493972

***cyclic*-OOPN**

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

P	-0.96043600	-0.01216100	-0.00005300

O 0.37745500 -1.05151300 0.00011300
N 0.23106300 1.08147000 0.00014200
O 1.22118300 0.12802800 -0.00013700
Zero-point correction= 0.010923 (Hartree/Particle)
Thermal correction to Energy= 0.014353
Thermal correction to Enthalpy= 0.015297
Thermal correction to Gibbs Free Energy= -0.015193
Sum of electronic and zero-point Energies= -546.479601
Sum of electronic and Thermal Energies= -546.476172
Sum of electronic and Thermal Enthalpies= -546.475227
Sum of electronic and Thermal Free Energies= -546.505717

(O=)PN(=O)
B3LYP/6-311++G(3df, 3pd)
P -0.19585200 0.75010800 0.00000000
O -0.19585200 -0.46795100 -1.11650400
N 0.86734300 -0.53777300 0.00000000
O -0.19585200 -0.46795100 1.11650400
Zero-point correction= 0.009335 (Hartree/Particle)
Thermal correction to Energy= 0.013242
Thermal correction to Enthalpy= 0.014186
Thermal correction to Gibbs Free Energy= -0.017114
Sum of electronic and zero-point Energies= -546.506435
Sum of electronic and Thermal Energies= -546.502528
Sum of electronic and Thermal Enthalpies= -546.501584
Sum of electronic and Thermal Free Energies= -546.532884

triplet *cyclic*-ONP(=O)
B3LYP/6-311++G(3df, 3pd)
P 0.29354400 0.11292100 0.36230300
O 1.56351600 -0.07346400 -0.36387200
O -1.05482900 -0.73698800 -0.07909000
N -1.21038000 0.68425800 -0.27012200
Zero-point correction= 0.009113 (Hartree/Particle)
Thermal correction to Energy= 0.013199
Thermal correction to Enthalpy= 0.014143
Thermal correction to Gibbs Free Energy= -0.018585
Sum of electronic and zero-point Energies= -546.523389
Sum of electronic and Thermal Energies= -546.519303
Sum of electronic and Thermal Enthalpies= -546.518359
Sum of electronic and Thermal Free Energies= -546.551087

singlet O_2NP
B3LYP/6-311++G(3df, 3pd)
O 0.00000000 1.09701200 -0.99422300
O 0.00000000 -1.09701200 -0.99422300
N 0.00000000 0.00000000 -0.42598300
P 0.00000000 0.00000000 1.25929700
Zero-point correction= 0.010636 (Hartree/Particle)
Thermal correction to Energy= 0.013934
Thermal correction to Enthalpy= 0.014878
Thermal correction to Gibbs Free Energy= -0.015184
Sum of electronic and zero-point Energies= -546.461134
Sum of electronic and Thermal Energies= -546.457836

Sum of electronic and Thermal Enthalpies= -546.456892
Sum of electronic and Thermal Free Energies= -546.486954

triplet O_2NP
B3LYP/6-311++G(3df, 3pd)

O	0.00000000	1.08667800	-1.04500500
O	0.00000000	-1.08667800	-1.04500500
N	0.00000000	0.00000000	-0.48868600
P	0.00000000	0.00000000	1.34272600

Zero-point correction= 0.011116 (Hartree/Particle)
Thermal correction to Energy= 0.015044
Thermal correction to Enthalpy= 0.015989
Thermal correction to Gibbs Free Energy= -0.016280
Sum of electronic and zero-point Energies= -546.480778
Sum of electronic and Thermal Energies= -546.476850
Sum of electronic and Thermal Enthalpies= -546.475906
Sum of electronic and Thermal Free Energies= -546.508174

***cyclic*-O_2N(≡P)**
B3LYP/6-311++G(3df, 3pd)

O	0.00000000	0.75245900	-1.30426400
O	0.00000000	-0.75245900	-1.30426400
N	0.00000000	0.00000000	-0.10560200
P	0.00000000	0.00000000	1.44049600

Zero-point correction= 0.008209 (Hartree/Particle)
Thermal correction to Energy= 0.011915
Thermal correction to Enthalpy= 0.012859
Thermal correction to Gibbs Free Energy= -0.017715
Sum of electronic and zero-point Energies= -546.371962
Sum of electronic and Thermal Energies= -546.368257
Sum of electronic and Thermal Enthalpies= -546.367312
Sum of electronic and Thermal Free Energies= -546.397886

triplet *cis*-OPON
B3LYP/6-311++G(3df, 3pd)

P	-0.70527500	-0.48778300	0.00001600
O	-1.24443700	0.86953100	-0.00001500
O	1.00861600	-0.46204400	-0.00003400
N	1.78081200	0.57955100	0.00002300

Zero-point correction= 0.008689 (Hartree/Particle)
Thermal correction to Energy= 0.013088
Thermal correction to Enthalpy= 0.014033
Thermal correction to Gibbs Free Energy= -0.019655
Sum of electronic and zero-point Energies= -546.554201
Sum of electronic and Thermal Energies= -546.549802
Sum of electronic and Thermal Enthalpies= -546.548858
Sum of electronic and Thermal Free Energies= -546.582545

triplet *trans*-OPON
B3LYP/6-311++G(3df, 3pd)

P	-0.55796600	-0.47628200	0.00004500
O	-1.65654600	0.48371900	-0.00012200
O	0.88449900	0.45875300	0.00019600
N	2.07798200	-0.05650700	-0.00018000

Zero-point correction= 0.008616 (Hartree/Particle)
Thermal correction to Energy= 0.013126
Thermal correction to Enthalpy= 0.014070
Thermal correction to Gibbs Free Energy= -0.019739
Sum of electronic and zero-point Energies= -546.552416
Sum of electronic and Thermal Energies= -546.547905
Sum of electronic and Thermal Enthalpies= -546.546961
Sum of electronic and Thermal Free Energies= -546.580770

CO

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

O	0.00000000	0.00000000	0.48191000
C	0.00000000	0.00000000	-0.64254600

Zero-point correction= 0.005050 (Hartree/Particle)
Thermal correction to Energy= 0.007411
Thermal correction to Enthalpy= 0.008355
Thermal correction to Gibbs Free Energy= -0.014066
Sum of electronic and zero-point Energies= -113.351743
Sum of electronic and Thermal Energies= -113.349382
Sum of electronic and Thermal Enthalpies= -113.348438
Sum of electronic and Thermal Free Energies= -113.370858

CO_2

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

C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.15901700
O	0.00000000	0.00000000	-1.15901700

Zero-point correction= 0.011723 (Hartree/Particle)
Thermal correction to Energy= 0.014335
Thermal correction to Enthalpy= 0.015279
Thermal correction to Gibbs Free Energy= -0.008964
Sum of electronic and zero-point Energies= -188.648677
Sum of electronic and Thermal Energies= -188.646065
Sum of electronic and Thermal Enthalpies= -188.645121
Sum of electronic and Thermal Free Energies= -188.669364

NO

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

N	0.00000000	0.00000000	-0.61047300
O	0.00000000	0.00000000	0.53416400

Zero-point correction= 0.004509 (Hartree/Particle)
Thermal correction to Energy= 0.006870
Thermal correction to Enthalpy= 0.007814
Thermal correction to Gibbs Free Energy= -0.015473
Sum of electronic and zero-point Energies= -129.935394
Sum of electronic and Thermal Energies= -129.933032
Sum of electronic and Thermal Enthalpies= -129.932088
Sum of electronic and Thermal Free Energies= -129.955376

O_2

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

O	0.00000000	0.00000000	0.60164900
O	0.00000000	0.00000000	-0.60164900

Zero-point correction= 0.003748 (Hartree/Particle)

Thermal correction to Energy= 0.006111
Thermal correction to Enthalpy= 0.007055
Thermal correction to Gibbs Free Energy= -0.016214
Sum of electronic and zero-point Energies= -150.375741
Sum of electronic and Thermal Energies= -150.373378
Sum of electronic and Thermal Enthalpies= -150.372433
Sum of electronic and Thermal Free Energies= -150.395702

OPN

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

O	0.00000000	0.00000000	1.42028000
P	0.00000000	0.00000000	-0.04334900
N	0.00000000	0.00000000	-1.53028700

Zero-point correction= 0.007017 (Hartree/Particle)
Thermal correction to Energy= 0.010371
Thermal correction to Enthalpy= 0.011316
Thermal correction to Gibbs Free Energy= -0.015766
Sum of electronic and zero-point Energies= -471.328161
Sum of electronic and Thermal Energies= -471.324807
Sum of electronic and Thermal Enthalpies= -471.323862
Sum of electronic and Thermal Free Energies= -471.350944

PN

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

P	0.00000000	0.00000000	0.47127600
N	0.00000000	0.00000000	-1.00987800

Zero-point correction= 0.003207 (Hartree/Particle)
Thermal correction to Energy= 0.005575
Thermal correction to Enthalpy= 0.006519
Thermal correction to Gibbs Free Energy= -0.017423
Sum of electronic and zero-point Energies= -396.113491
Sum of electronic and Thermal Energies= -396.111123
Sum of electronic and Thermal Enthalpies= -396.110179
Sum of electronic and Thermal Free Energies= -396.134121

PO

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

P	0.00000000	0.00000000	0.51391600
O	0.00000000	0.00000000	-0.96359300

Zero-point correction= 0.002866 (Hartree/Particle)
Thermal correction to Energy= 0.005240
Thermal correction to Enthalpy= 0.006184
Thermal correction to Gibbs Free Energy= -0.018562
Sum of electronic and zero-point Energies= -416.600583
Sum of electronic and Thermal Energies= -416.598209
Sum of electronic and Thermal Enthalpies= -416.597265
Sum of electronic and Thermal Free Energies= -416.622010

HNCO

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

C	0.00000000	0.04967600	0.00000000
N	-0.38576100	-1.09744000	0.00000000
H	-1.34673500	-1.39123300	0.00000000
O	0.50588300	1.09690800	0.00000000

Zero-point correction= 0.021332 (Hartree/Particle)
Thermal correction to Energy= 0.024567
Thermal correction to Enthalpy= 0.025512
Thermal correction to Gibbs Free Energy= -0.001546
Sum of electronic and zero-point Energies= -168.730499
Sum of electronic and Thermal Energies= -168.727263
Sum of electronic and Thermal Enthalpies= -168.726319
Sum of electronic and Thermal Free Energies= -168.753377

HOCN

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

C	0.18051500	-0.00282400	0.00000000
O	-1.11046300	-0.11033800	0.00000000
H	-1.53309000	0.75937300	0.00000000
N	1.33338700	0.02003900	0.00000000

Zero-point correction= 0.021555 (Hartree/Particle)
Thermal correction to Energy= 0.024891
Thermal correction to Enthalpy= 0.025835
Thermal correction to Gibbs Free Energy= -0.001557
Sum of electronic and zero-point Energies= -168.684713
Sum of electronic and Thermal Energies= -168.681376
Sum of electronic and Thermal Enthalpies= -168.680432
Sum of electronic and Thermal Free Energies= -168.707824

HCNO

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

H	0.00000000	0.00000000	2.23509200
N	0.00000000	0.00000000	0.02051500
O	0.00000000	0.00000000	-1.17882700
C	0.00000000	0.00000000	1.17532000

Zero-point correction= 0.019909 (Hartree/Particle)
Thermal correction to Energy= 0.023623
Thermal correction to Enthalpy= 0.024568
Thermal correction to Gibbs Free Energy= -0.002157
Sum of electronic and zero-point Energies= -168.621670
Sum of electronic and Thermal Energies= -168.617956
Sum of electronic and Thermal Enthalpies= -168.617011
Sum of electronic and Thermal Free Energies= -168.643736

O_2NNCO

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

O	-1.98922400	-0.55137300	0.00048500
N	0.22204400	-0.79376400	-0.00045700
O	-0.78020000	1.25122800	-0.00005100
C	1.32842100	-0.24345800	-0.00008600
O	2.41447400	0.13221400	0.00032300
N	-0.95503400	0.05150700	-0.00033400

Zero-point correction= 0.024760 (Hartree/Particle)
Thermal correction to Energy= 0.029860
Thermal correction to Enthalpy= 0.030804
Thermal correction to Gibbs Free Energy= -0.004556
Sum of electronic and zero-point Energies= -373.255074
Sum of electronic and Thermal Energies= -373.249974
Sum of electronic and Thermal Enthalpies= -373.249030

Sum of electronic and Thermal Free Energies= -373.284390

(O=)NNOC(=O)

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

O	0.06257200	1.04018200	0.00005200
O	-2.07871900	0.03476900	-0.00001100
N	-0.05955500	-1.04676600	0.00006600
C	0.97168400	-0.04561600	-0.00010600
O	2.14202500	-0.04203600	0.00001200
N	-0.91717700	-0.09460800	-0.00003600

Zero-point correction= 0.025060 (Hartree/Particle)
Thermal correction to Energy= 0.029612
Thermal correction to Enthalpy= 0.030556
Thermal correction to Gibbs Free Energy= -0.002838
Sum of electronic and zero-point Energies= -373.236897
Sum of electronic and Thermal Energies= -373.232345
Sum of electronic and Thermal Enthalpies= -373.231401
Sum of electronic and Thermal Free Energies= -373.264795

N_2O

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

O	0.00000000	0.00000000	1.10925900
N	0.00000000	0.00000000	-0.07321600
N	0.00000000	0.00000000	-1.19450900

Zero-point correction= 0.011194 (Hartree/Particle)
Thermal correction to Energy= 0.013864
Thermal correction to Enthalpy= 0.014808
Thermal correction to Gibbs Free Energy= -0.010099
Sum of electronic and zero-point Energies= -184.722154
Sum of electronic and Thermal Energies= -184.719484
Sum of electronic and Thermal Enthalpies= -184.718539
Sum of electronic and Thermal Free Energies= -184.743447

TS5

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

O	2.05751700	-0.09947600	0.00000000
N	-0.02918700	-1.02308400	0.00000000
O	0.16571900	1.09002600	0.00000000
C	-1.04608400	-0.14331300	0.00000000
O	-2.18456500	0.04084100	0.00000000
N	0.88163500	-0.03280900	0.00000000

Zero-point correction= 0.024383 (Hartree/Particle)
Thermal correction to Energy= 0.028603
Thermal correction to Enthalpy= 0.029547
Thermal correction to Gibbs Free Energy= -0.003393
Sum of electronic and zero-point Energies= -373.232737
Sum of electronic and Thermal Energies= -373.228517
Sum of electronic and Thermal Enthalpies= -373.227573
Sum of electronic and Thermal Free Energies= -373.260513

TS6

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

O	0.25963900	-1.11764900	0.00005300

O	-2.13198600	-0.09613800	-0.00004300
N	-0.14478200	1.03193000	-0.00004900
C	0.98499600	-0.03155500	0.00002400
O	2.14033600	0.18299000	0.00004100
N	-1.00577400	0.17317100	-0.00003000

Zero-point correction= 0.023591 (Hartree/Particle)
Thermal correction to Energy= 0.028066
Thermal correction to Enthalpy= 0.029010
Thermal correction to Gibbs Free Energy= -0.004444
Sum of electronic and zero-point Energies= -373.234722
Sum of electronic and Thermal Energies= -373.230247
Sum of electronic and Thermal Enthalpies= -373.229302
Sum of electronic and Thermal Free Energies= -373.262757