Supplementary Material for PCCP

Table S1. Geometry (Bond Lengths in Å, Angles in °) of the energetically most stable **sha** structures.

Parameter	z,z,z,z-isomer (**1**)	e,e,z,z-isomer(**2**)	z,z,e,e/z-isomer (**3**)
C_2-C_3	1.383	1.388	1.383
C_2-C_6	1.407	1.401	1.412
C_3-C_4	1.401	1.394	1.400
C_4-C_5	1.384	1.391	1.382
C_5-C_7	1.403	1.395	1.403
C_6-C_7	1.417	1.405	1.426
C_6-C_8	1.473	1.496	1.476
C_7-O_{10}	1.343	1.375	1.340
C_8-O_9	1.246	1.235	1.241
C_8-N_1	1.365	1.353	1.386
N_1-O_{16}	1.398	1.392	1.405
C_2-H_{11}	1.084	1.083	1.078
C_3-H_{12}	1.083	1.083	1.083
C_4-H_{13}	1.084	1.084	1.085
C_5-H_{14}	1.083	1.086	1.083
O_{10}-H_{15}	0.983	0.963	0.988
O_{16}-H_{18}	0.979	0.980	0.966
N_1-H_{17}	1.009	1.009	1.015
$O_9 \cdots H_{15}$	1.740	-	1.657
$O_9 \cdots H_{18}$	1.955	1.969	-
$O_{10} \cdots H_{17}$	-	1.989	-
C_2-C_3-C_4	119.2	119.4	119.6
C_2-C_6-C_7	118.9	118.0	118.0
C_3-C_4-C_5	120.8	120.0	120.5
C_4-C_5-C_7	120.4	120.3	120.6
C_2-C_3-H_{12}	120.3	120.1	119.9
C_3-C_4-H_{13}	119.8	120.5	120.0
C_4-C_5-H_{14}	121.6	120.3	121.7
C_6-C_2-H_{11}	119.6	117.1	119.1
C_6-C_8-O_9	123.3	122.5	121.7

C_7-O_{10}-H_{15}	107.9	110.2	107.2
C_8-N_1-H_{17}	120.8	124.5	111.9
C_8-N_1-O_{16}	116.0	116.7	123.1
N_1-O_{16}-H_{18}	102.1	101.2	104.3
$O_9\cdots H_{15}$-O_{10}	145.7	-	146.7
$O_9\cdots H_{18}$-O_{16}	118.6	118.8	-
$O_{10}\cdots H_{17}$-N_1	-	122.9	-
C_2-C_6-C_8-N_1	9.0	171.0	-12.5
C_4-C_5-C_7-O_{10}	-179.0	-179.6	179.4
C_6-C_7-O_{10}-H_{15}	-3.7	179.2	2.7
H_{11}-C_2-C_3-H_{12}	-1.4	-0.3	1.1
H_{12}-C_3-C_4-H_{13}	-0.7	0.0	0.5
H_{13}-C_4-C_5-H_{14}	0.1	0.2	-0.1
H_{17}-N_1-O_{16}-H_{18}	146.0	162.7	102.6
O_9-C_8-N_1-O_{16}	-8.7	-8.3	-158.1

Table S2. Definition of internal coordinates used in the normal mode analysis of **sh**a (the numbering scheme is presented in Fig. 1).

Definition [a]	Vibration [a]
ν_1	ν (C_8-N_1)
ν_2	ν (N_1-O_{16})
ν_3	ν (N_1-H_{17})
ν_4	ν (C_2-C_3)
ν_5	ν (C_2-C_6)
ν_6	ν (C_2-H_{11})
ν_7	ν (C_3-C_4)
ν_8	ν (C_3-H_{12})
ν_9	ν (C_4-C_5)
ν_{10}	ν (C_4-H_{13})
ν_{11}	ν (C_5-C_7)
ν_{12}	ν (C_5-H_{14})
ν_{13}	ν (C_6-C_7)
ν_{14}	ν (C_6-C_8)
ν_{15}	ν (C_7-O_{10})

ν_{16}	ν (C_8-O_9)
ν_{17}	ν (O_{10}-H_{15})
ν_{18}	ν (O_{16}-H_{18})
δ_1	δ (C_3-C_2-H_{11}) - δ (C_6-C_2-H_{11})
δ_2	δ (C_2-C_3-H_{12}) - δ (C_4-C_3-H_{12})
δ_3	δ (C_3-C_4-H_{13}) - δ (C_5-C_4-H_{13})
δ_4	δ (C_4-C_5-H_{14}) - δ (C_7-C_5-H_{14})
δ_5	δ (C_5-C_7-O_{10}) - δ (C_6-C_7-O_{10})
δ_6	δ (C_2-C_6-C_8) - δ (C_7-C_6-C_8)
δ_7	δ (C_3-C_4-C_5) - δ (C_4-C_5-C_7) + δ (C_5-C_7-C_6)-δ (C_2-C_3-C_4) + δ (C_3-C_2-C_6) - δ (C_2-C_6-C_7)
δ_8	2 δ (C_3-C_2-C_6) - δ (C_2-C_3-C_4) - δ (C_2-C_6-C_7) - δ (C_3-C_4-C_5) + 2 δ (C_4-C_5-C_7) - δ (C_5-C_7-C_6)
δ_9	δ (C_2-C_3-C_4) - δ (C_2-C_6-C_7) - δ (C_3-C_4-C_5) + δ (C_5-C_7-C_6)
δ_{10}	δ (C_7-O_{10}-H_{15})
δ_{11}	δ (N_1-O_{16}-H_{18})
δ_{12}	2 δ (C_6-C_8-O_9) - δ (N_1-C_8-O_9) - δ (C_6-C_8-N_1)
δ_{13}	δ (N_1-C_8-O_9)- δ (C_6-C_8-N_1)
δ_{14}	2 δ (C_8-N_1-O_{16}) - δ (C_8-N_1-H_{17}) - δ (O_{16}-N_1- H_{17})
δ_{15}	δ (C_8-N_1-H_{17}) - δ (O_{16}-N_1- H_{17})
γ_1	γ (C_3-C_2(-H_{11})-C_6)
γ_2	γ (C_2-C_3(-H_{12})-C_4)
γ_3	γ (C_3-C_4(-H_{13})-C_5)
γ_4	γ (C_4-C_5(-H_{14})-C_7)
γ_5	γ (C_5-C_7(-O_{10})-C_6)
γ_6	γ (C_2-C_6(-C_7)-C_8)
γ_7	γ (N_1-C_8(-C_6)-O_9)
γ_8	γ (C_8-N_1(-H_{17})-O_{16})
τ_1	τ (C_2-C_6-C_7-C_5) - τ (C_2-C_3-C_4-C_5) - τ (C_3-C_2-C_6-C_7) + τ (C_3-C_4-C_5-C_7) + τ (C_4-C_3-C_2-C_6) - τ (C_4-C_5-C_7-C_6)
τ_2	τ (C_4-C_3-C_2-C_6) - τ (C_3-C_2-C_6-C_7) - τ (C_3-C_4-C_5-C_7) + τ (C_4-C_5-C_7-C_6)
τ_3	2 τ (C_2-C_3-C_4-C_5) + 2 τ (C_2-C_6-C_7-C_5) - τ (C_3-C_2-C_6-C_7) - τ (C_3-C_4-C_5-C_7) - τ (C_4-C_3-C_2-C_6) - τ (C_4-C_5-C_7-C_6)
τ_4	τ (C_5-C_7-O_{10}-H_{15}) + τ (C_6-C_7-O_{10}-H_{15})
τ_5	τ (C_2-C_6-C_8-N_1) + τ (C_2-C_6-C_8-O_9) + τ (C_7-C_6-C_8-N_1) + τ (C_7-C_6-C_8-O_9)
τ_6	τ (C_6-C_8-N_1-H_{17}) + τ (C_6-C_8-N_1-O_{16}) + τ (H_{16}-N_1-C_8-O_9) + τ (H_{17}-N_1-C_8-O_9)
τ_7	τ (C_8-N_1-O_{16}-H_{18}) + τ (H_{17}-N_1-O_{16}-H_{18})

[a] ν, δ, γ, and τ denote stretching, in-plane bending, out-of plane bending, and torsion vibrations, respectively.

Table S3. Assignments of experimental spectrum recorded after photolysis of **sha** in an Ar matrix at 20 K. Harmonic frequencies (in cm^{-1}) and integral intensities (in km/mol) are calculated at B3LYP/6-311++G(d,p) level. Relative intensities are given in parenthesis. Assignment of bands is based on Potential Energy Distributions (PEDs) of normal modes (in percent), defined in Table 2 of supporting information.

ν_{exp} (cm^{-1})	$\nu_{calc}^{a,b}$ (cm^{-1})	Assignment[c]
501 (3)	508 (0.9)	δ_5 (40), δ_6 *as.*[c] (10), δ_{12} *as.* (6)
528 (7)	523 (3.5)	τ_3 (33), γ_5 (22), τ_1 *as.* (20), γ_2 (10), γ_4 (5)
556 (1)	559 (0.2)	δ_8 (41), δ_9 *as.* (19), δ_6 (9), ν_5 (7), ν_{15} (5)
671 (5)	669 (3.7)	δ_8 (34), δ_9 (14), δ_{12} *as.* (10), τ_1 *as.* (8), ν_{13} *as.* (8), ν_{14} *as.* (6)
700 (8)	675 (3.1)	τ_1 (56), γ_5 (18), γ_7 *as.* (6), γ_3 (5)
735 (2)	735 (0.8)	τ_1 (22), γ_7 (22), τ_4 *as.* (17), γ_6 (14), γ_5 (12), γ_2 *as.* (7)
751 (46), 745	742 (48.1)	τ_4 (27), γ_2 *as.* (25), γ_1 (11), γ_5 (11), γ_3 *as.* (11), γ_4 *as.* (9)
788 (5)	770 (4.5)	τ_4 (28), γ_7 (22), γ_6 (12), γ_2 (10), γ_3 (8), γ_1 *as.* (7), τ_1 (6)
829 (11)	824 (5.7)	δ_7 (20), ν_{15} *as.* (17), δ_9 *as.* (13), ν_{13} *as.* (13), ν_{11} *as.* (13), δ_{13} *as.* (5)
857 (2)	849 (0.4)	γ_4 (43), γ_1 (21), τ_1 *as.* (8), γ_5 *as.* (8), γ_3 (7)
910 (6)	899 (2.2)	δ_7 (26), δ_{14} *as.* (22), δ_{13} (14), δ_{12} *as.* (10), ν_{16} (5)
-	932 (0.6)	γ_1 (47), γ_2 (30), γ_4 *as.* (11), τ_2 *as.* (7)
956 (1)	963 (0.1)	γ_3 (55), γ_4 *as.* (19), γ_2 *as.* (13), τ_1 (8)
1018 (45)	1013 (36.0)	ν_2 (45), ν_1 (12), δ_7 *as.* (11), δ_{14} *as.* (10), δ_{11} *as.* (6)
1037 (4)	1035 (2.9)	ν_7 (47), δ_4 (13), ν_9 (12), ν_4 (7), δ_1 (6)
1105 (9)	1103 (5.7)	δ_7 (19), ν_2 (18), ν_{11} (10), ν_4 *as.* (9), δ_3 *as.* (8)
1146 (17)	1145 (8.7)	δ_4 (24), δ_3 *as.* (24), ν_2 *as.* (8), ν_9 (7), ν_{14} (6), ν_1 (6)
-	1168 (0.1)	δ_2 (43), ν_4 (15), δ_3 *as.* (9), δ_1 (8)
1221 (31)	1221 (19.7)	ν_{11} (19), δ_{10} (12), δ_4 *as.* (12), δ_1 (11), δ_{15} *as.* (9), ν_{13} *as.* (8), ν_1 (8), δ_5 *as.* (5)
1257 (27)	1257 (14.1)	ν_5 (28), ν_{15} *as.* (22), δ_1 *as.* (15), ν_{14} *as.* (8)

1294 (20)	1287 (14.2)	δ_{15} (27), ν_{15} (14), ν_{14} *as.* (10), δ_{11} (9), δ_7 (9)
1323 (18)	1322 (6.2)	ν_{13} (20), ν_9 (14), ν_{15} *as.* (12), δ_4 *as.* (9), ν_4 (8), ν_5 *as.* (6), δ_2 *as.* (6)
1353 (41), 1350 (23)	1377 (36.3)	δ_{10} (22), δ_1 *as.* (11), δ_{11} *as.* (9), ν_4 (9), ν_9 (9), ν_1 (7), δ_3 (6), ν_7 *as.* (5)
1408 (100)	1406 (86.1)	δ_{11} (23), δ_{10} (19), ν_{14} (15), ν_1 *as.* (7)
1444 (33)	1451 (4.6)	δ_3 (15), δ_2 (14), ν_4 *as.* (10), ν_{16} (10), ν_{15} *as.* (10), ν_{11} (9), ν_{13} (7), δ_4 (7)
1489 (22)	1488 (18.3)	δ_1 (16), δ_2 *as.* (16), δ_4 (13), ν_7 *as.* (12), δ_{10} (10), ν_5 (9)
1529 (18)	1527 (21.2)	δ_{11} (30), δ_{15} *as.* (29), ν_1(16)
1590 *sh* [d]	1582 (6.1)	ν_9 (21), ν_7 *as.* (14), ν_{13} *as.* (11), δ_3 (11), δ_{10} *as.* (11), ν_{16} *as.* (7), ν_5 (6), δ_8 *as.* (5)
1604 (28)	1602 (30.1)	ν_{16} (28), ν_4 (17), ν_{11} (8), ν_{13} *as.* (8), ν_7 *as.* (6)
1650 (94)	1643 (59.9)	ν_{16} (24), ν_{11} *as.* (11), ν_5 (9), ν_9 (7), δ_9 (6), ν_4 *as.* (6), ν_{14} *as.* (6)
3066 *sp* [e]	3107 (0.1)	ν_6 (39), ν_{10} (35), ν_8 *as.* (22)
3078 *sp*	3113 (2.4)	ν_6 (48), ν_{10} *as.* (45), ν_{12} (6)
3115 *sp*	3131 (2.7)	ν_8 (46), ν_{12} *as.* (45), ν_6 (8)
3115 *sp*	3137 (1.5)	ν_{12} (45), ν_8 (31), ν_{10} (19)
3341 (39)	3376 (100.0)	ν_{17} (100)
3463 (21),	3506 (15.6)	ν_{18} (97)
3475 (11),	3552 (21.1)	ν_3 (97)

[a] B3LYP/6-311++G(d,p) of the z,z,z,z conformer, frequencies scaled uniformly by 0.98, [b] Only contributions more than 5 % were considered, [c] *as.* – an asymmetric vibration, [d] *sh.* – shoulder, [e] *sp.* – superimposed bands; calculations of integral intensity not possible.

Table S4. Assignments of experimental spectrum recorded after photolysis of **sha** in an Ar matrix at 12 K. Harmonic frequencies (in cm^{-1}) and integral intensities (in km/mol) are calculated at B3LYP/6-311++G(d,p) level. Relative intensities are given in parenthesis. Assignment of bands is based on Potential Energy Distributions (PEDs) of normal modes (in percent), defined in Table 2 of supporting information.

ν_{exp} (cm^{-1})	ν_{calc} (cm^{-1})$^{a-c}$	Species	Assignment^{d}
723 (0.19)^{e}	737 (0.19)	A	ν C_6-N_1 (22), δ_8 *as.*^{f} (15), ν_{13} (14), ν_1 (9), ν_5 (9), δ C_2-C_6-N_1 - δ C_7-C_6-N_1 (8), λ C_6-N_1-C_8-O_9 *as.* (6)
754 (0.47)^{e}	743 (0.54)	A	γ_2 (36), γ_3 (26), γ_1 *as.* (20), γ_4 (11)
749 (0.16)^{e}	757 (0.18)	B	γ_2 (38), γ_3 (21), γ_1 *as.* (21), γ_4 (12)
836 (0.14)	833 (0.08)	A	δ_7 (36), ν_{15} *as.* (20), δ_9 *as.* (19), ν_{11} *as.* (7)
997 (0.10)	1028 (0.05)	B	ν_7 (47), ν_9 (13), δ_4 (11), ν_4 (9), δ_1 (7)
	1029 (0.12)	A	ν_7 (40), ν_9 (16), δ_4 (11), ν_4 (10), δ_1 (8)
1082 (0.26)	1076 (0.16)	A	δ_7 (38), ν_{11} (12), ν C_6-N_1 *as.* (10), δ_1 *as.* (6), δ_3 *as.* (5), ν_4 *as.* (5)
1151 (0.15)	1137 (0.12)	A	δ_4 (24), δ_3 *as.* (15), ν_4 *as.* (13), ν C_6-N_1 (10), ν_9 (8), ν_1 (5), δ_2 *as.* (5)
	1137 (0.23)	B	ν_{16} (41), δ_4 (14), ν_5 *as.* (8), ν_{11} *as.* (5), ν_{14} (5)
1203 (1.00)	1199 (1.00)	A	δ_{10} (40), ν_{11} (13), ν_{13} *as.* (10), δ_4 *as.* (7), δ_1 (6)
1210 (0.18)^{e}	1224 (0.46)	B	δ_{10} (29), ν_{14} (14), ν_{13} *as.* (12), ν_1 (9), δ_7 *as.* (9) ν_4 *as.* (7)
1254 (0.06)^{e}	1251 (0.15)	B	ν_{15} (36), ν_5 *as.* (22), δ_1 (9), δ_3 (5)
1260 (0.26)^{e}	1252 (0.63)	A	ν_{15} (32), ν_5 *as.* (22), δ_1 (19), δ C_2-C_6-N_1 - δ C_7-C_6-N_1 (6), δ_7 (5)
1304 (0.55)^{e}	1296 (0.33)	A	ν_9 (16), ν_{13} (15), δ_4 *as.* (15), ν_{15} *as.* (12), ν_5 *as.* (9), ν_4 (7), δ_2 *as.* (7), ν_7 *as.* (5)
1326 (0.15)	1326 (0.05)	B	ν_9 (14), δ_4 *as.* (14), ν_{13} (14), ν_{15} *as.* (9), δ_2 *as.* (9), ν_4 *as.* (7)
1344 (0.19)	1344 (0.20)	A	δ_{10} (23), δ_3 (13), ν_7 *as.* (11), ν_4 (10), δ_1 *as.* (10), ν_5 *as.* (9), ν_{11} *as.* (7), ν_9 (7), ν_{13} (5)
1349 (0.03)^{e}	1353 (0.09)	B	δ_{10} (27), δ_1 *as.* (12), ν_4 (11), δ_3 (10), ν_9 (9), ν_7 *as.* (8)
1428 (0.27)	1445 (0.12)	A	ν_{16} (19), ν_1 (16), δ_2 (12), δ_1 *as.* (11), ν C_6-N_1 *as.* (9), δ_4 *as.* (7), δ_{10} *as.* (6), ν_7 (6)
1456 (0.08)	1468 (0.14)	A	δ_3 (19), δ_2 (17), ν_4 *as.* (16), ν_{11} (10), ν_{15} *as.* (6), δ C_2-C_6-N_1 - δ C_7-C_6-N_1 (5)
1477 (0.12)^{e}	1473 (0.12)	B	δ_2 (21), δ_3 (14), ν_4 *as.* (13), ν_5 *as.* (9), ν_{11} (8), ν_{15} *as.* (6)
1482 (0.29)^{e}	1482 (0.28)	B	δ_1 (20), δ_4 (19), ν_{13} (12), ν_7 *as.* (9), δ_2 *as.* (8), ν_{15} *as.* (8)
1527 (0.89)^{e}	1517 (0.83)	A	ν C_6-N_1 (21), ν_{16} *as.* (11), δ_1 *as.* (10), δ_4 *as.* (9), ν_1 *as.* (8), ν_5 *as.* (7), ν_7 (5), ν_{15} (5)

1598 (0.07) [e]	1582 (0.17)	B	ν_7 (20), ν_{13} (20), ν_9 *as.* (15), δ_3 *as.* (10), δ_8 (9), ν_5 *as.* (6)
1589 (1.30) [e]	1595 (0.40)	A	ν_9 (20), ν_{13} *as.* (18), ν_7 *as.* (16), ν_5 (12), δ_3 (8), δ_8 *as.* (7)
1617 (0.17) [e]	1624 (0.23)	B	ν_4 (21), ν_{11} (19), ν_9 *as.* (12), ν_5 *as.* (11), δ_9 *as.* (10), δ_1 *as.* (7), δ_4 (5)
1789 (0.98)	1750 (1.00)	B	ν_1 (62), ν_{14} *as.* (24), ν_{16} (7)
2258 (17.49) [e]	2307 (12.10)	A	ν_1 (49), ν_{16} *as.* (49)
3214 (0.01)	3115 (0.05)	A	ν_{10} (52), ν_6 *as.* (38), ν_{12} *as.* (9)
3228 (0.11)	3130 (0.07)	A	ν_8 (51), ν_{12} *as.* (37), ν_6 (10)
3383 (2.61)	3691 (0.69)	A	ν_{17} (100)
3425 (0.91)	3643 (0.41)	B	ν_{17} (100)

[a] B3LYP/6-311++G(d,p) of A and B, frequencies scaled uniformly by factor of 0.98, [b] In A and B structure the intensities are relative to the 1199 and 1750 cm^{-1} experimental band integral intensity, respectively, [c] The theoretical bands of relative intensity ≥ 0.05 were included, [d] Only contributions more than 5 % were considered, [e] Intensity is not reliable due to overlapped bands, [f] as. – an asymmetric vibration.