Electronic Supplementary Material for PCCP

On the nature of the unusually long OO bond in HO_3 and HO_4 radicals.

Alex Mansergas,[a] Josep M. Anglada, [a,]* Santiago Olivella,[a] Manuel F. Ruiz-López[b] and Marilia Martins-Costa[b]

[a] Theoretical and Computational Chemistry Group, Departament de Química Orgànica Biològica, Institut d'Investigacions Químiques i Ambientals de Barcelona, IIQAB – CSIC, C/ Jordi Girona 18, E-08034 Barcelona, Spain.

[b] Equipe de Chimie et Biochimie Théoriques, UMR CNRS-UHP No.7565 Nancy - University, BP 239, 54506 Vandoeuvre-les-Nancy, France

E-mail: anglada@iiqab.csic.es

(Supplementary information)

Table S1. Optimized geometrical parameters computed at different levels of theory for the ***trans*-HO_3** radical.[a]

Method [b]	$d(O_1O_2)$	$D(O_2O_3)$	$d(O_3H_4)$	$A(O_1O_2O_3)$	$A(O_2O_3H_4)$	$D(O_1O_2O_3H_4)$
B3LYP/B2	1.232	1.545	0.971	110.3	98.6	0.0
QCISD/B2	1.244	1.522	0.967	109.1	98.4	0.0
CCSD(T)/B1	1.244	1.540	0.971	109.6	98.1	0.0
CCSD(T)/B2	1.247	1.512	0.969	109.3	98.4	0.0
CCSD(T)/B3	1.251	1.513	0.972	109.2	98.4	0.0
CASSCF(7,7)/B2	1.316	1.459	0.946	108.2	100.9	91.0
CASSCF(13,13)/B2	1.227	1.742	0.975	110.8	94.8	0.0
CASSCF(15,13)/B2	1.232	1.660	0.948	110.5	96.8	0.0
CASSCF(19,15)/B2	1.223	1.758	0.976	110.8	94.2	0.0
MRCI/B1 [c]	1.233	1.647	0.960	107.4	96.6	0.0
CASPT2 (13,11)/B2	1.211	1.739	0.972	110.5	94.9	0.0
EXP [d]	1.225	1.688	0.972	111.0	90.0	0.0
MRCI+Q/B3 [d]	1.225	1.677	0.972	110.2	95.9	0.0

[a] Distances are in angstroms and angles in degrees. The atom numbering is as shown in Figure 1.

[b] B1 stands for 6-311+G(d,p), B2 stands for 6-311+G(2df,2p) and B3 stands for aug-cc-pVTZ.

[c] MRCI done over the CASSCF(13,13) set of molecular orbitals.

[d] Values taken from reference[4].

Table S2. Calculated topological properties (in a.u.) at the *bcp* in the **HO_3** and **HO_4** radicals [a].

x-y	r_x	r_y	$\rho(r_{bcp})$	$\nabla^2\rho(r_{bcp})$	$\varepsilon(r_{bcp})$	$H_b(r_{bcp})$
			***trans*-HO_3**			
H_4-O_3	0.36010	1.46698	0.37241	-2.76199	0.03589	-0.7633
	(0.33826)	(1.45385)	(0.38997)	(-2.94052)	(0.03734)	(-0.8199)
O_3-O_2	1.44191	1.43422	0.23851	0.16977	0.12061	-0.1471
	(1.57650)	(1.56091)	(0.16356)	(0.31533)	(0.12671)	(-0.0700)
O_2-O_1	1.14006	1.21182	0.48209	-0.32452	0.00031	-0.5150
	(1.13935)	(1.18916)	(0.50169)	(-0.39095)	(0.00019)	(-0.5783)
			***cis*-HO_4**			
O_2-O_1	1.17039	1.13314	0.51845	-0.43209	0.00889	-0.6169
	(1.17007)	(1.13355)	(0.52054)	(-0.46457)	(0.01290)	(-0.6194)
O_3-O_2	1.59329	1.60311	0.15543	0.31696	0.17903	-0.0621
	(1.59148)	(1.60454)	(0.15157)	(0.37607)	(0.18781)	(-0.0562)
O_4-O_3	1.28255	1.26978	0.36612	-0.08548	0.02835	-0.3319
	(1.28252)	(1.27068)	(0.36771)	(-0.11026)	(0.03593)	(-0.3329)
H_5-O_4	0.34620	1.48142	0.37310	-2.81723	0.03420	-0.7832
	(0.35244)	(1.47499)	(0.37782)	(-2.83035)	(0.03681)	(-0.7838)
O_4-O_1	2.29715	2.27371	0.02618	0.13433	0.95375	-0.0045
	(2.29905)	(2.26876)	(0.02521)	(0.13911)	(0.94771)	(-0.0054)
ring			0.02584	0.16265		
			(0.02489)	(0.16573)		
			***trans*-HO_4**			

O_2-O_1	1.19446	1.13991	0.49574	-0.35693	0.00075	-0.5688
O_3-O_2	1.49261	1.49874	0.20695	0.24271	0.18813	-0.1194
O_4-O_3	1.29729	1.30485	0.34325	-0.06411	0.00957	-0.2978
H_5-O_4	0.34689	1.47813	0.37449	-2.82069	0.03824	-0.8577

[a] Computed employing the first order density matrix obtained at QCISD/6311+G(2df,2p) and MRCI/6311+G(2df,2p) (in parenthesis) levels of theory. Atom numbering is as shown in Figure 1.