Supplementary Information
Theoretical studies on thermal stability of alkyl-substituted 1,2-dioxetanes

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Table S1. AM1 output parameters for the 1,2-dioxetanes studied

Molecule	V_M, cm^3 mol^{-1}	d(O-O), pm	d(C-C), pm	d(O-O)/d(C-C)	ω, °	μ, D	E_{HOMO}, eV	E_{LUMO}, eV
1	36.4	133.9	153.9	0.870	0.00	3.17	-10.58	2.06
2	47.5	133.7	154.5	0.866	-0.50	3.28	-10.53	2.06
3	58.5	133.5	155.0	0.861	0.00	3.35	-10.47	2.03
4	58.6	133.5	155.1	0.861	-0.86	3.36	-10.47	2.08
5	58.3	133.5	155.2	0.860	-0.01	3.38	-10.46	2.07
6	69.3	133.3	155.9	0.855	0.51	3.43	-10.40	2.05
7	79.8	133.1	156.8	0.849	-0.10	3.46	-10.34	2.04
8	69.4	133.5	155.1	0.861	0.09	3.39	-10.44	2.05
9	69.6	133.5	155.1	0.861	-0.77	3.39	-10.44	2.11
10	69.4	133.5	155.2	0.860	-0.12	3.32	-10.42	2.09
11	80.4	133.3	156.0	0.855	0.84	3.44	-10.37	2.08
12	80.5	133.5	155.1	0.861	0.06	3.41	-10.44	2.05
13	91.5	133.5	155.1	0.861	0.06	3.44	-10.43	2.05
14	80.2	133.5	155.2	0.860	0.11	3.32	-10.41	2.08
15	80.5	133.5	155.1	0.861	-0.69	3.32	-10.41	2.13
16	80.3	133.4	155.3	0.859	0.62	3.31	-10.38	2.12
17	90.5	133.5	155.3	0.860	-0.16	3.21	-10.37	2.12
18	80.3	133.5	155.2	0.860	0.08	3.32	-10.41	2.08
19	80.7	133.5	155.1	0.861	-1.11	3.42	-10.42	2.14
20	80.4	133.5	155.2	0.860	-0.03	3.25	-10.39	2.11
21	123.2	132.9	157.8	0.842	-3.53	3.32	-10.19	2.12
22	91.5	133.6	155.1	0.861	1.11	3.35	-10.39	2.16
23	91.3	133.4	155.3	0.859	0.76	3.25	-10.34	2.14
24	102.8	133.5	155.1	0.861	-1.08	3.46	-10.41	2.14
25	102.5	133.5	155.2	0.860	0.03	3.23	-10.39	2.10
26	124.9	133.5	155.1	0.861	-1.05	3.51	-10.40	2.14
27	124.6	133.4	155.3	0.859	-0.28	3.38	-10.38	2.12
28	178.8	132.4	157.8	0.839	-9.80	2.97	-9.88	2.24
29	192.9	132.2	158.9	0.832	3.16	2.86	-9.87	2.19
30	186.7	132.4	157.8	0.839	-5.46	2.96	-9.89	2.24

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Table S2. PM3 output parameters for the 1,2-dioxetanes studied

Molecule	V_M, cm^3 mol^{-1}	d(O-O), pm	d(C-C), pm	d(O-O)/d(C-C)	ω, °	μ, D	E_{HOMO}, eV	E_{LUMO}, eV
1	36.5	157.4	152.9	1.029	-0.02	2.66	-10.97	0.32
2	47.6	157.1	153.6	1.022	0.07	2.77	-11.02	0.42
3	58.5	156.8	154.2	1.017	0.00	2.84	-11.05	0.51
4	58.7	156.7	154.4	1.015	0.27	2.86	-11.06	0.52
5	58.5	156.6	154.7	1.012	-0.01	2.87	-11.02	0.53
6	69.3	156.3	155.4	1.006	0.01	2.92	-11.05	0.62
7	79.6	155.6	156.9	0.992	0.02	2.93	-11.03	0.75
8	69.2	156.8	154.3	1.016	0.22	2.90	-11.00	0.52
9	69.7	156.7	154.4	1.015	0.28	2.87	-11.03	0.53
10	69.5	156.6	154.8	1.012	-0.18	2.84	-10.97	0.55
11	80.2	156.2	155.6	1.004	-0.12	2.92	-11.00	0.64
12	80.3	156.8	154.3	1.016	0.10	2.91	-11.00	0.52
13	91.3	156.8	154.3	1.016	0.18	2.92	-11.00	0.52
14	80.0	156.7	154.5	1.014	0.21	2.85	-10.96	0.53
15	80.5	156.7	154.5	1.014	0.02	2.83	-10.99	0.54
16	79.9	156.5	154.9	1.010	0.89	2.86	-10.92	0.56
17	90.2	156.8	154.6	1.014	-2.23	2.80	-10.91	0.55
18	80.2	156.6	154.4	1.015	-0.21	2.83	-10.95	0.54
19	80.6	156.8	154.5	1.015	0.44	2.89	-11.00	0.52
20	80.5	156.5	154.8	1.011	0.02	2.80	-10.93	0.56
21	122.5	155.5	157.7	0.986	-1.79	2.94	-10.83	0.76
22	91.4	156.6	154.5	1.014	-0.59	2.85	-10.96	0.54
23	91.0	156.4	155.0	1.009	0.79	2.84	-10.87	0.57
24	102.7	156.8	154.5	1.015	0.58	2.92	-11.00	0.52
25	102.6	156.5	154.8	1.011	0.02	2.79	-10.95	0.55
26	124.7	156.8	154.5	1.015	0.56	2.95	-11.00	0.52
27	124.2	156.5	154.9	1.011	0.30	2.92	-10.94	0.55
28	178.2	152.9	158.6	0.964	-9.08	2.72	-10.40	1.15
29	192.6	152.9	160.3	0.954	8.13	2.59	-10.38	1.09
30	186.3	152.7	158.2	0.966	-2.32	2.71	-10.37	1.14

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Table S3. B3LYP/6-31G(d) output parameters for the 1,2-dioxetanes studied

Molecule	V_M, cm^3 mol^{-1}	d(O-O), pm	d(C-C), pm	d(O-O)/d(C-C)	ω, °	μ, D	E_{HOMO}, eV	E_{LUMO}, eV
1	36.4	149.0	152.1	0.979	0.00	3.25	-6.27	-0.20
2	47.4	149.2	152.3	0.979	-12.38	3.31	-6.25	-0.06
3	58.4	148.9	153.1	0.972	0.00	3.29	-6.13	0.01
4	58.5	149.1	152.7	0.976	-12.68	3.34	-6.17	0.08
5	58.4	148.8	153.7	0.968	0.00	3.33	-6.10	0.10
6	69.3	149.0	154.0	0.967	13.80	3.30	-6.10	0.20
7	80.0	148.9	155.7	0.957	-17.03	3.20	-6.06	0.30
8	69.5	148.9	153.2	0.972	-2.68	3.36	-6.10	0.05
9	69.6	149.0	152.9	0.975	-9.87	3.41	-6.13	0.10
10	69.5	148.9	153.5	0.970	-8.95	3.24	-6.11	0.08
11	80.5	149.0	154.2	0.967	15.12	3.35	-6.09	0.21
12	80.6	148.9	153.2	0.972	-8.18	3.43	-6.11	0.07
13	91.7	148.9	153.1	0.973	-5.38	3.45	-6.09	0.06
14	80.3	148.8	153.2	0.971	-7.58	3.23	-6.12	0.03
15	80.5	149.0	152.8	0.975	-9.54	3.29	-6.13	0.07
16	80.4	149.0	153.6	0.970	12.65	3.26	-6.13	0.10
17	90.7	148.8	153.4	0.970	5.41	3.09	-6.13	0.00
18	80.5	148.9	153.1	0.973	-10.25	3.26	-6.13	0.05
19	80.7	148.8	153.1	0.972	-0.46	3.40	-6.08	0.11
20	80.6	148.7	153.6	0.968	0.00	3.19	-6.07	0.05
21	139.6	148.8	156.6	0.950	18.99	3.07	-6.02	0.34
22	91.6	148.8	153.0	0.972	4.66	3.25	-6.09	0.07
23	91.5	149.0	153.6	0.970	13.74	3.17	-6.13	0.07
24	103.0	148.9	153.1	0.973	-5.65	3.57	-6.05	0.15
25	102.8	148.7	153.6	0.968	0.00	3.12	-6.05	0.07
26	142.0	148.9	152.9	0.974	-7.15	3.28	-6.08	0.12
27	141.7	148.7	153.6	0.968	-0.11	3.09	-6.06	0.04
28	199.5	148.0	157.9	0.938	-23.10	2.72	-5.93	0.20
29	215.5	147.2	158.6	0.928	19.73	2.68	-5.93	0.17
30	205.9	148.2	157.3	0.942	22.20	2.76	-5.91	0.20

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Table S4. X-Ray structural parameters of the peroxidic ring and activation energies of selected 1,2-dioxetanes

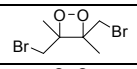
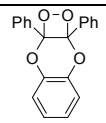
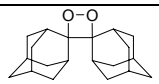
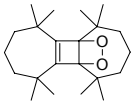
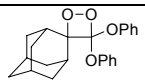
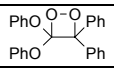
	d(O-O), pm	d(C-C), pm	dP/dC	ω, °	Ref	$\Delta G^{\ddagger}$, kJ mol^{-1}	Ref
	144.0	151.0	0.954	15.3	1	26.2	2
	152.1	158.0	0.963	0.8	3	26.1	3
	148.0	154.9	0.955	21.3	4,5	32.9	6
	148.8	155.2	0.959	0.0	7	27.3	8
	147.0	148.0	0.993	11.7	1	29.2	9
	150.5	155.0	0.971	9.6	1	26.7	9

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Table S5. Experimental activation parameters for the 1,2-dioxetanes studied

Molecule	E_a, kJ mol^{-1}	$\Delta G^{\ddagger}$, kJ mol^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, eu	Ref
1	95.0	97.1	79.1	-12.6	[10]
2	95.4	97.9	90.0	-5.5	[10]
3	102.5	101.3	94.1	-5.1	[10]
4	100.8	100.4	90.0	-7.4	[10]
5	103.8	101.3	90.4	-7.6	[10]
6	108.8	104.6	97.9	-4.7	[10]
7	116.3	108.4	104.2	-2.8	[10]
8	102.5	99.6	99.6	-1.3	[11]
9	103.3	100.8	100.4	-0.4	[12]
10	103.8	100.8	100.8	0.0	[12]
11	103.3	103.8	100.4	-2.3	[13]
12	102.9	100.0	100.0	0.0	[11]
13	102.1	100.0	99.2	-0.5	[11]
14	104.6	101.3	101.7	0.4	[11]
15	107.9	100.4	105.0	3.3	[12]
16	109.2	101.7	106.3	3.3	[12]
17	107.9	103.8	105.0	0.8	[11]
18	104.2	102.5	101.3	-0.8	[13]
19	104.2	102.5	101.3	-0.8	[14]
20	102.5	101.3	100.0	-0.7	[15]
21	128.9	115.1	122.6	8.0	[16,17]
22	106.3	105.4	103.3	-1.5	[12]
23	105.0	101.7	102.1	0.2	[12]
24	104.6	102.1	101.7	-0.2	[14]
25	102.5	100.4	99.6	-0.7	[14]
26	105.0	102.9	102.1	-0.6	[14]
27	102.9	102.5	100.0	-1.7	[14]
28	149.0	134.3	146.0	8.0	[18]
29	126.8	130.5	123.8	-4.5	[19]
30	144.8	137.7	141.4	2.9	[6]

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Table S6. HF/6-31G(d) output parameters for the methyl series

Molecule	d(O-O), pm	d(C-C), pm	ω, °	μ, D	E_{HOMO}, eV	E_{LUMO}, eV
1	142.1	151.7	0.0	3.72	-0.41	0.23
2	142.1	152.0	-6.4	3.73	-0.40	0.22
3	142.0	152.6	0.0	3.69	-0.40	0.21
4	142.1	152.3	-8.7	3.72	-0.40	0.23
5	142.0	153.0	-0.3	3.72	-0.40	0.22
6	142.0	153.3	11.9	3.67	-0.40	0.22
7	142.0	154.7	16.0	3.56	-0.39	0.21

Table S7. MP2/6-31G(d) output parameters for the methyl series

Molecule	d(O-O), pm	d(C-C), pm	ω, °	μ, D	E_{HOMO}, eV	E_{LUMO}, eV
1	152.0	150.9	19.2	3.85	-0.43	0.19
2	152.0	151.3	17.7	3.82	-0.42	0.19
3	152.0	151.7	18.3	3.84	-0.42	0.19
4	151.9	151.7	16.5	3.76	-0.42	0.20
5	152.2	152.0	-19.5	3.86	-0.42	0.20
6	152.1	152.6	-18.7	3.76	-0.41	0.20
7	152.3	153.7	21.4	3.74	-0.41	0.20

Table S8. B3LYP/6-31+G(d,p) output parameters for the methyl series.

Molecule	d(O-O), pm	d(C-C), pm	ω, °	μ, D	E_{HOMO}, eV	E_{LUMO}, eV
1	149.0	152.2	0.0	3.58	-0.24	-0.03
2	149.2	152.5	-12.5	3.64	-0.24	-0.03
3	148.9	153.2	-9.8	3.61	-0.24	-0.02
4	149.1	152.9	-12.8	3.70	-0.24	-0.02
5	148.8	153.8	-0.3	3.70	-0.24	-0.02
6	149.0	154.2	14.3	3.67	-0.24	-0.02
7	148.8	155.9	17.3	3.58	-0.24	-0.01

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Table S9. Linear coefficients A and B calculated from $\Delta G^{\ddagger} = A + B \cdot d(C\text{-}C)$ for the methyl series with d(C-C) predicted by several methods

Method	A	Error	B	Error	SD, kJ mol^{-1}
AM1	-526.3	46.3	4.0	0.3	0.7
PM3	-360.3	36.2	3.0	0.2	0.7
B3LYP/6-31G(d)	-375.8	46.2	3.1	0.3	0.9
HF/6-31G(d)	-481.5	56.5	3.8	0.4	0.9
MP2/6-31G(d)	-548.6	42.8	4.3	0.3	0.6
B3LYP/6-31+G(d,p)	-364.9	46.5	3.0	0.3	0.9

References

1. Adam, W.; Arias, L. A.; Zahn, A.; Zinner, K.; Peters, K.; Peters, E. M.; von Schnering, H. G. *Tetrahedron Lett.* **1982**, *23*, 3251.
2. Adam, W.; Sakanishi, K. *J. Am. Chem. Soc.* **1978**, *100*, 3935.
3. Adam, W.; Peters, E. M.; Peters, K.; Platsch, H.; Schmidt, E.; von Schnering, H. G.; Takayama, K. *J. Org. Chem.* **1984**, *49*, 3920.
4. Hess, J.; Vos, A. *Acta Crystallogr. Sect. B-Struct. Commun.* **1977**, *33*, 3527.
5. Numan, H.; Wieringa, J. H.; Wynberg, H.; Hess, J.; Vos, A. *J. Chem. Soc., Chem. Commun.* **1977**, 591.
6. Schuster, G. B.; Turro, N. J.; Steinmetzer, H. C.; Schaap, A. P.; Faler, G.; Adam, W.; Liu, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 7110.
7. Krebs, A.; Schmalstieg, H.; Jarchow, O.; Klaska, K. H. *Tetrahedron Lett.* **1980**, *21*, 3171.
8. Adam, W.; Zinner, K.; Krebs, A.; Schmalstieg, H. *Tetrahedron Lett.* **1981**, *22*, 4567.
9. Adam, W.; Encarnacion, L. A. A.; Zinner, K. *Chem. Ber.-Recl.* **1983**, *116*, 839.
10. Adam, W.; Baader, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 410.
11. Baumstark, A. L.; Dunams, T.; Catalani, L. H.; Bechara, E. J. H. *J. Org. Chem.* **1983**, *48*, 3713.
12. Baumstark, A. L.; Retter, C. A.; Tehrani, K.; Kellogg, C. *J. Org. Chem.* **1987**, *52*, 3308.
13. Baumstark, A. L.; Dunams, T. *J. Org. Chem.* **1982**, *47*, 3754.
14. Baumstark, A. L.; Dunams, T.; Roskamp, P. C.; Wilson, C. E. *J. Org. Chem.* **1983**, *48*, 261.
15. Baumstark, A. L.; Wilson, C. E. *Tetrahedron Lett.* **1979**, 2569.
16. Bechara, E. J. H.; Wilson, T. *J. Org. Chem.* **1980**, *45*, 5261.
17. Bechara, E. J. H.; Baumstark, A. L.; Wilson, T. *J. Am. Chem. Soc.* **1976**, *98*, 4648.
18. Lechtken, P. *Chem. Ber.* **1976**, *109*, 2862.
19. McCapra, F.; Beheshti, I. *J. Chem. Soc., Chem. Commun.* **1977**, 517.