Photoisomerization reactions of 4-methoxy- and 4-hydroxy-6-methyl-α-pyrones: an experimental matrix isolation and theoretical density functional theory study

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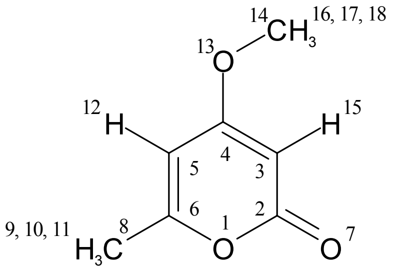
ELECTRONIC SUPPLEMENTARY INFORMATION



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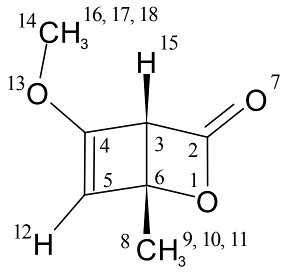

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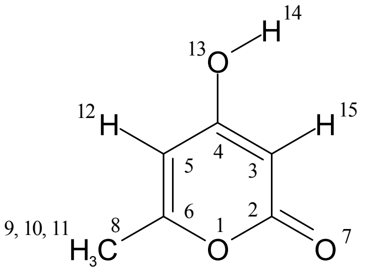
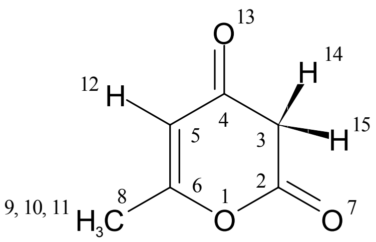
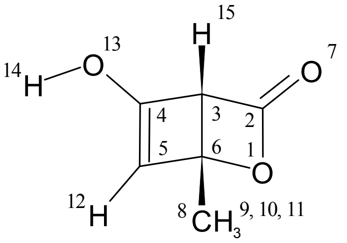


V



VI



VIII

Scheme S1. Atom numbering.

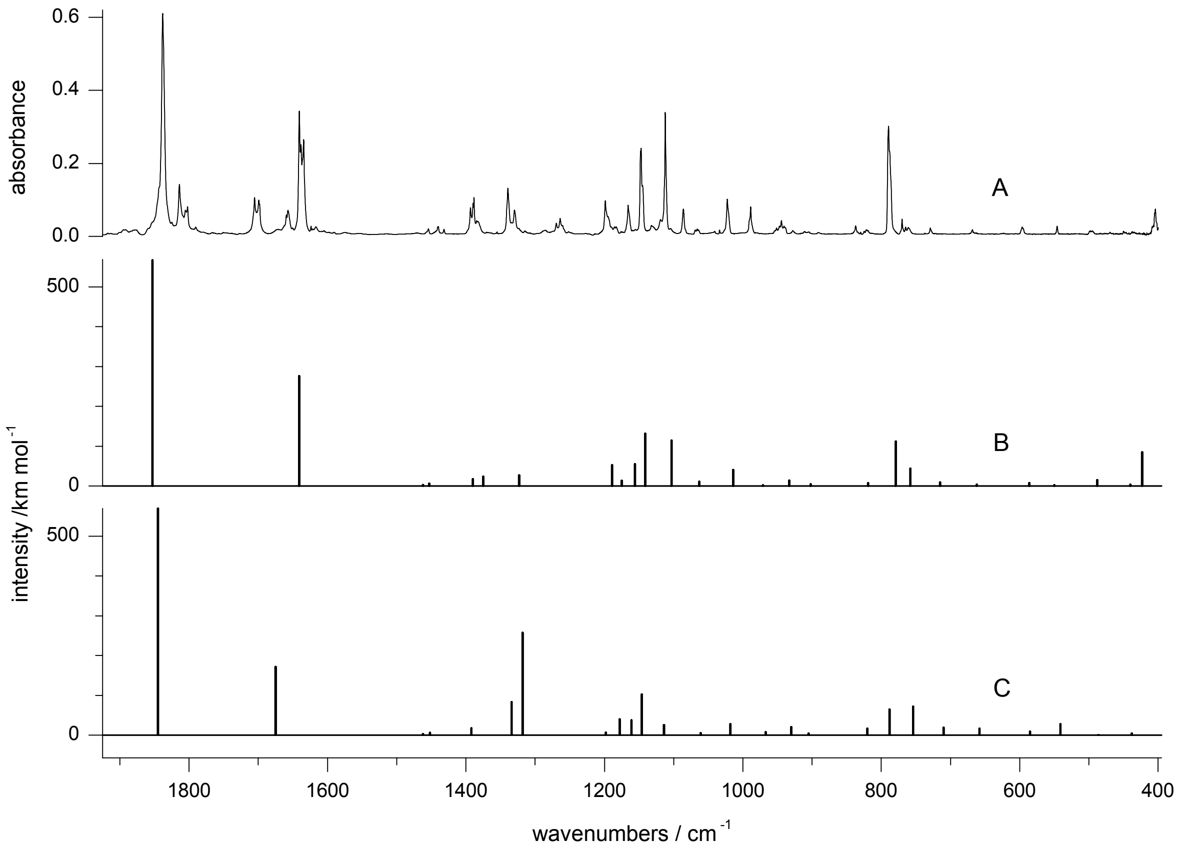


Figure S1. (A) Experimental spectrum recorded after UV (λ > 320 nm) irradiation of matrix isolated 4-hydroxy-6-methyl-α-pyrone; (B) the spectrum of the Dewar isomer **VIII** theoretically predicted at DFT(B3LYP)/6-311++G(d,p) level; (C) theoretical spectrum of the Dewar isomer **IX**. Theoretical wavenumbers were scaled by 0.98. Baseline of the experimental spectrum was corrected.

Table S1 Internal coordinates used in the normal mode analysis for the 4-hydroxy-6-methyl-α-pyrone and 4-methoxy-6-methyl-α-pyrone (Atom numbering as in Scheme S1)

$S_1 = r_{1,2}$		ν(O1-C2)
$S_2 = r_{2,3}$		ν(C2-C3)
$S_3 = r_{3,4}$		ν(C3=C4)
$S_4 = r_{4,5}$		ν(C4-C5)
$S_5 = r_{5,6}$		ν(C5=C6)
$S_6 = r_{6,1}$		ν(C6-O1)
$S_7 = r_{7,2}$		ν(C2=O7)
$S_8 = r_{8,6}$		ν(C8-C6)
$S_9 = (3^{-1/2})(r_{9,8} + r_{10,8} + r_{11,8})$		$\nu(CH_3)^{1}{}_{s}$
$S_{10} = (6^{-1/2})(2r_{11,8} - r_{10,8} - r_{9,8})$		$\nu(CH_3)^{1'}{}_{as}$
$S_{11} = (2^{-1/2})(r_{10,8} - r_{9,8})$		$\nu(CH_3)^{1''}{}_{as}$
$S_{12} = r_{12,5}$		ν(C5-H12)
$S_{13} = r_{13,4}$		ν(C4-O13)
$S_{14} = r_{14,13}$	hydroxy	ν(O13-H14)
$S_{14} = r_{14,13}$	methoxy	ν(O13-C14)
$S_{15} = r_{15,3}$		ν(C3-H15)
$S_{16} = (6^{-1/2})(\beta_{2,6,1} - \beta_{1,5,6} + \beta_{6,4,5} - \beta_{5,3,4} + \beta_{4,2,3} - \beta_{3,1,2})$		δ ring 1
$S_{17} = (12^{-1/2})(2\beta_{2,6,1} - \beta_{1,5,6} - \beta_{6,4,5} + 2\beta_{5,3,4} - \beta_{4,2,3} - \beta_{3,1,2})$		δ ring 2
$S_{18} = (1/2)(- \beta_{1,5,6} + \beta_{6,4,5} - \beta_{4,2,3} + \beta_{3,1,2})$		δ ring 3
$S_{19} = (2^{-1/2})(\beta_{7,1,2} - \beta_{7,3,2})$		δ(C2=O7)
$S_{20} = (2^{-1/2})(\beta_{8,1,6} - \beta_{8,5,6})$		δ(C6-C8)
$S_{21} = (6^{-1/2})(\beta_{9,10,8} + \beta_{10,11,8} + \beta_{11,9,8} - \beta_{9,6,8} - \beta_{10,6,8} - \beta_{11,6,8})$		$\delta(CH_3)^{1}{}_{s}$
$S_{22} = (6^{-1/2})(2\beta_{9,10,8} - \beta_{10,11,8} - \beta_{11,9,8})$		$\delta(CH_3)^{1'}{}_{as}$
$S_{23} = (2^{-1/2})(\beta_{10,11,8} - \beta_{11,9,8})$		$\delta(CH_3)^{1''}{}_{as}$
$S_{24} = (6^{-1/2})(2\beta_{11,6,8} - \beta_{10,6,8} - \beta_{9,6,8})$		$\gamma(CH_3)^{1'}{}_{as}$
$S_{25} = (2^{-1/2})(\beta_{10,6,8} - \beta_{9,6,8})$		$\gamma(CH_3)^{1''}{}_{as}$
$S_{26} = (2^{-1/2})(\beta_{12,6,5} - \beta_{12,4,5})$		δ(C5-H12)
$S_{27} = (2^{-1/2})(\beta_{13,5,4} - \beta_{13,3,4})$		δ(C4-O13)
$S_{28} = \beta_{14,4,13}$	hydroxy	δ(O13-H14)
$S_{28} = \beta_{14,4,13}$	methoxy	δ(O13-C14)
$S_{29} = (2^{-1/2})(\beta_{15,4,3} - \beta_{15,2,3})$		δ(C3-H15)

$S_{30} = (6^{-1/2})(\tau_{6,1,2,3} - \tau_{1,2,3,4} + \tau_{2,3,4,5} - \tau_{3,4,5,6} + \tau_{4,5,6,1} - \tau_{5,6,1,2})$		γ ring 1
$S_{31} = (12^{-1/2})(2\tau_{6,1,2,3} - \tau_{1,2,3,4} - \tau_{2,3,4,5} + 2\tau_{3,4,5,6} - \tau_{4,5,6,1} - \tau_{5,6,1,2})$		γ ring 2
$S_{32} = (1/2)(\tau_{1,2,3,4} - \tau_{2,3,4,5} + \tau_{4,5,6,1} - \tau_{5,6,1,2})$		γ ring 3
$S_{33} = (6^{-1/2})(\tau_{11,8,6,5} + \tau_{11,8,6,1} + \tau_{10,8,6,5} + \tau_{10,8,6,1} + \tau_{9,8,6,5} + \tau_{9,8,6,1})$		*twist* $(CH_3)^1$
$S_{34} = (2^{-1/2})(\tau_{14,13,4,5} + \tau_{14,13,4,3})$	hydroxy	τ(C4-OH)
$S_{34} = (2^{-1/2})(\tau_{14,13,4,5} + \tau_{14,13,4,3})$	methoxy	$\tau(C4\text{-}OCH_3)$
$S_{35} = \gamma_{7,3,2,1}$		γ(C2=O7)
$S_{36} = \gamma_{8,1,6,5}$		γ(C6-C8)
$S_{37} = \gamma_{12,6,5,4}$		γ(C5-H12)
$S_{38} = \gamma_{13,5,4,3}$		γ(C4-O13)
$S_{39} = \gamma_{15,4,3,2}$		γ(C3-H15)
$S_{40} = (3^{-1/2})(r_{18,14} + r_{16,14} + r_{17,14})$	methoxy	$\nu(CH_3)^2{}_s$
$S_{41} = (1/2)(2r_{17,14} - r_{16,14} - r_{18,14})$	methoxy	$\nu(CH_3)^{2'}{}_{as}$
$S_{42} = (2^{-1/2})(r_{16,14} - r_{18,14})$	methoxy	$\nu(CH_3)^{2''}{}_{as}$
$S_{43} = (6^{-1/2})(\beta_{18,16,14} + \beta_{16,17,14} + \beta_{17,18,14} - \beta_{18,13,14} - \beta_{16,13,14} - \beta_{17,13,14})$	methoxy	$\delta(CH_3)^2{}_s$
$S_{44} = (6^{-1/2})(2\beta_{18,16,14} - \beta_{16,17,14} - \beta_{17,18,14})$	methoxy	$\delta(CH_3)^{2'}{}_{as}$
$S_{45} = (2^{-1/2})(\beta_{16,17,14} - \beta_{17,18,14})$	methoxy	$\delta(CH_3)^{2''}{}_{as}$
$S_{46} = (6^{-1/2})(2\beta_{17,13,14} - \beta_{16,13,14} - \beta_{18,13,14})$	methoxy	$\gamma(CH_3)^{2'}{}_{as}$
$S_{47} = (2^{-1/2})(\beta_{16,13,14} - \beta_{18,13,14})$	methoxy	$\gamma(CH_3)^{2''}{}_{as}$
$S_{48} = (3^{-1/2})(\tau_{18,14,13,4} + \tau_{17,14,13,4} + \tau_{16,14,13,4})$	methoxy	*twist* $(CH_3)^2$

$r_{i,j}$ is the distance between atoms A_i and A_j; $\beta_{i,j,k}$ is the angle between vectors A_kA_i and A_kA_j; $\tau_{i,j,k,l}$ is the dihedral angle between the plane defined by A_i, A_j, A_k and the plane defined by A_j, A_k, A_l atoms; $\gamma_{i,j,k,l}$ is the angle between the vector A_kA_i and the plane defined by atoms A_j, A_k, A_l.

Table S2 Experimental wavenumbers $\tilde{\nu}$ (cm^{-1}), integral intensities *I* (relative) of the infrared bands of 4-methoxy-6-methyl-α-pyrone compared with theoretical wavenumbers $\tilde{\nu}$ (cm^{-1}), absolute intensities Ath (km mol^{-1}) and potential energy distributions (%) calculated for form **I**.

Experimental		Calculated			
Ar matrix		DFT(B3LYP)/6-311++G(d,p)			
$\tilde{\nu}$	*I*	$\tilde{\nu}$ ^{a}	Ath	sym.	PED^{b}
3018 3014	17				
2979	20	3174	1	A’	ν(C3-H15)(100)
2951	14	3162	1	A’	ν(C5-H12)(99)
		3086	14	A’	ν(CH$_3$)$^{2'}_{as}$ (92)
2937 2915	7	3067	10	A’	ν(CH$_3$)$^{1'}_{as}$ (97)
		3030	24	A’’	ν(CH$_3$)$^{2''}_{as}$ (100)
2886	6	3028	5	A’’	ν(CH$_3$)$^{1''}_{as}$ (100)
2875	2	2975	11	A’	ν(CH$_3$)$^{1}_{s}$ (97)
2859	17	2964	32	A’	ν(CH$_3$)$^{2}_{s}$ (92)
2836 2826	6				
1790	6				
1762 1757	712	1770	751	A’	ν(O7=C2)(81)
1725	16				
1664 1657	190	1650	233	A’	ν(C5=C6)(52) + ν(C3=C4)(13)
1584 1582 1576	244	1566	245	A’	ν(C3=C4)(49) + ν(C5=C6)(11) + ν(C4-C5)(11)
1462	115	1473	8	A’	δ(CH$_3$)$^{2'}_{as}$ (83)
		1464	76	A’	δ(CH$_3$)$^{1'}_{as}$ (39) + δ(CH$_3$)$^{2}_{s}$ (21) + ν(C4-C5)(10)
		1463	11	A’’	δ(CH$_3$)$^{2''}_{as}$ (94)
1443	16	1449	11	A’	δ(CH$_3$)$^{2}_{s}$ (55) + δ(CH$_3$)$^{1'}_{as}$ (36)
1434	11	1441	9	A’’	δ(CH$_3$)$^{1''}_{as}$ (91)
1406	82	1404	88	A’	δ(C3-H15)(18) + ν(C4-C5)(18) + δ(CH$_3$)$^{2}_{s}$ (17) +δ(CH$_3$)$^{1'}_{as}$ (12)
1385	4	1390	2	A’	δ(CH$_3$)$^{1}_{s}$ (91)
1363	4				
1351	5				
1322 1319	46	1320	57	A’	δ(C5-H12)(21) + ν(O1-C6)(21) + ν(C3-C2)(13)
1250	196	1244	205	A’	ν(C4-O13)(31) + δ(C3-H15)(26) + γ(CH$_3$)$^{2'}_{as}$ (10)
1201	4	1195	9	A’	γ(CH$_3$)$^{2'}_{as}$ (39) + δ(C5-H12)(18) + δ(C3-H15)(15)
1163 1153	71	1157	41	A’	γ(CH$_3$)$^{2'}_{as}$ (32) + δ(C5-H12)(18) + ν(C4-O13)(14)
		1146	1	A’’	γ(CH$_3$)$^{2''}_{as}$ (93)
1146 1140 1121	70	1120	51	A’	ν(C3-C2)(33) + δ(C3-H15)(16) + ν(C8-C6)(12)
1047 1046 1041	71	1042	50	A’	ν(O13-C14)(33)+δ(C5-H12)(18)+ν(C4-C5)(12)+γ(CH$_3$)$^{1'}_{as}$ (11)
		1041	3	A’’	γ(CH$_3$)$^{1''}_{as}$ (78) + γ(C6-C8)(14)
1027 1024	28	1013	20	A’	γ(CH$_3$)$^{1'}_{as}$ (51) + ν(O1-C6)(18) + ν(O13-C14)(13)
984	8	973	7	A’	δ ring 1 (37) + ν(C4-C5)(23) + ν(O1-C6)(15)
943	44	932	33	A’	ν(O13-C14)(32) + ν(C8-C6)(19) + ν(C4-O13)(12)
856 852 849	67	811	70	A’	ν(O1-C2)(54) + δ ring 1 (15)
814	72	801	67	A’’	γ(C5-H12)(57) + γ(C3-H15)(39) + γ(C4-O13)(20)
800	2	795	4	A’’	γ(C3-H15)(48) + γ(C5-H12)(44) + γ(C2=O7)(20)

		705	1	A’’	γ(C2=O7)(61) + γ ring 1 (29) + γ(C3-H15)(15)
684	3	672	2	A’’	γ(C4-O13)(50) + γ ring 1 (29)
634	9	623	8	A’	ν(O1-C2)(12) + δ(C4-O13)(11) + δ(O13-C14)(11) +δring 1 (11)
561	3	548	5	A’	δ(C2=O7)(35) + ν(C8-C6)(10)
		542	0.09	A’’	γ(C6-C8)(50) + γ ring 3 (20) + γ(C4-O13)(17)
541	9	535	5	A’	δ ring 3 (68) + δ(O13-C14)(12)
		479	1	A’	δ ring 2 (42)
		397	0.2	A’	δ ring 2 (30) + δ(O13-C14)(22) + δ(C2=O7)(13)
		289	1	A’	δ(C6-C8) (60)
		245	3	A’’	*twist* $(\mathrm{CH_3})^2$ (62) + γ ring 2 (20)
		216	0.04	A’’	τ(C4-$\mathrm{OCH_3}$)(30) +γ ring 2 (18) +*twist* $(\mathrm{CH_3})^2$ (15) +γ ring 3 (12) + *twist* $(\mathrm{CH_3})^1$ (11) + γ(C6-C8)(11)
		211	6	A’	δ(C4-O13)(48) + δ(O13-C14)(31)
		178	4	A’’	γ ring 3 (57) + *twist* $(\mathrm{CH_3})^2$ (20) + γ ring 2 (14) + γ(C6-C8) (10)
		152	0.08	A’’	*twist* $(\mathrm{CH_3})^1$ (61) + γ ring 1 (18)
		138	0.1	A’’	γ ring 1 (36) + *twist* $(\mathrm{CH_3})^1$ (22) + γ ring 2 (22)
		94	4	A’’	τ(C4-$\mathrm{OCH_3}$) (56) + γ ring 2 (25)

[a] Theoretical positions of absorption bands were scaled by a factor of 0.98.

[b] PED’s lower than 10% are not included. Definition of internal coordinates is given in Table S1.

Table S3 Internal coordinates used in the normal mode analysis for the 4-hydroxy-6-methyl-1-oxa-2-oxobicyclo[2.2.0]hex-4-ene and 4-methoxy-6-methyl-1-oxa-2-oxobicyclo[2.2.0]hex-4-ene. (Atom numbering as in Scheme S1)

$S_1 = r_{1,2}$		ν(O1-C2)
$S_2 = r_{2,3}$		ν(C2-C3)
$S_3 = r_{3,4}$		ν(C3-C4)
$S_4 = r_{4,5}$		ν(C4=C5)
$S_5 = r_{5,6}$		ν(C5-C6)
$S_6 = r_{6,1}$		ν(O1-C6)
$S_7 = r_{6,3}$		ν(C3-C6)
$S_8 = r_{7,2}$		ν(C2=O7)
$S_9 = r_{8,6}$		ν(C6-C8)
$S_{10} = (3^{-1/2})(r_{9,8} + r_{10,8} + r_{11,8})$		$\nu(CH_3)^{1}{}_{s}$
$S_{11} = (6^{-1/2})(2r_{10,8} - r_{9,8} - r_{11,8})$		$\nu(CH_3)^{1'}{}_{as}$
$S_{12} = (2^{-1/2})(r_{9,8} - r_{11,8})$		$\nu(CH_3)^{1''}{}_{as}$
$S_{13} = r_{12,5}$		ν(C5-H12)
$S_{14} = r_{13,4}$		ν(C4-O13)
$S_{15} = r_{14,13}$	hydroxy	ν(O13-H14)
$S_{15} = r_{14,13}$	methoxy	ν(O13-C14)
$S_{16} = r_{15,3}$		ν(C3-H15)
$S_{17} = (1/2)(\beta_{2,6,1} + \beta_{2,6,3} - \beta_{1,3,2} - \beta_{1,3,6})$		δ ring 1
$S_{18} = (1/2)(\beta_{2,4,3} + \beta_{2,4,5} - \beta_{3,5,6} - \beta_{3,5,4})$		δ ring 2
$S_{19} = (2^{-1/2})(\beta_{7,1,2} - \beta_{7,3,2})$		δ(C2=O7)
$S_{20} = \beta_{8,3,6}$		δ(C6-C8)
$S_{21} = (6^{-1/2})(\beta_{9,10,8} + \beta_{10,11,8} + \beta_{11,9,8} - \beta_{9,6,8} - \beta_{10,6,8} - \beta_{11,6,8})$		$\delta(CH_3)^{1}{}_{s}$
$S_{22} = (6^{-1/2})(2\beta_{9,11,8} - \beta_{10,11,8} - \beta_{10,9,8})$		$\delta(CH_3)^{1'}{}_{as}$
$S_{23} = (2^{-1/2})(\beta_{10,11,8} - \beta_{10,9,8})$		$\delta(CH_3)^{1''}{}_{as}$
$S_{24} = (6^{-1/2})(2\beta_{10,6,8} - \beta_{9,6,8} - \beta_{11,6,8})$		$\gamma(CH_3)^{1'}{}_{as}$
$S_{25} = (2^{-1/2})(\beta_{9,6,8} - \beta_{11,6,8})$		$\gamma(CH_3)^{1''}{}_{as}$
$S_{26} = (2^{-1/2})(\beta_{12,6,5} - \beta_{12,4,5})$		δ(C5-H12)
$S_{27} = (2^{-1/2})(\beta_{13,3,4} - \beta_{13,5,4})$		δ(C4-O13)
$S_{28} = \beta_{14,4,13}$	hydroxy	δ(O13-H14)
$S_{28} = \beta_{14,4,13}$	methoxy	δ(O13-C14)
$S_{29} = \beta_{15,6,3}$		δ(C3-H15)

$S_{30} = (1/2)(\tau_{6,1,2,3} - \tau_{1,2,3,6} + \tau_{2,3,6,1} - \tau_{3,6,1,2})$		τ ring 1
$S_{31} = (1/2)(\tau_{6,5,4,3} - \tau_{5,4,3,6} + \tau_{4,3,6,5} - \tau_{3,6,5,4})$		τ ring 2
$S_{32} = (2^{-1/2})(\tau_{8,6,3,4} + \tau_{8,6,3,2})$		γ(C6-C8)
$S_{33} = (2^{-1/2})(\tau_{15,3,6,1} + \tau_{15,3,6,5})$		γ(C3-H15)
$S_{34} = (2^{-1/2})(\tau_{2,3,6,5} - \tau_{4,3,6,1})$		τ butterfly
$S_{35} = (6^{-1/2})(\tau_{9,8,6,1} + \tau_{9,8,6,5} + \tau_{10,8,6,1} + \tau_{10,8,6,5} + \tau_{11,8,6,1} + \tau_{11,8,6,5})$		*twist* $(CH_3)^1$
$S_{36} = (2^{-1/2})(\tau_{14,13,4,3} + \tau_{14,13,4,5})$	hydroxy	τ(C4-OH)
$S_{36} = (2^{-1/2})(\tau_{14,13,4,3} + \tau_{14,13,4,5})$	methoxy	$\tau(C4\text{-}OCH_3)$
$S_{37} = \gamma_{7,1,2,3}$		γ(C2=O7)
$S_{38} = \gamma_{12,6,5,4}$		γ(C5-H12)
$S_{39} = \gamma_{13,5,4,3}$		γ(C4-O13)
$S_{40} = (3^{-1/2})(r_{18,14} + r_{16,14} + r_{17,14})$	methoxy	$\nu(CH_3)^{2}_{s}$
$S_{41} = (6^{-1/2})(2r_{18,14} - r_{16,14} - r_{17,14})$	methoxy	$\nu(CH_3)^{2'}_{as}$
$S_{42} = (2^{-1/2})(r_{16,14} + r_{17,14})$	methoxy	$\nu(CH_3)^{2''}_{as}$
$S_{43} = (6^{-1/2})(\beta_{18,16,14} + \beta_{16,17,14} + \beta_{17,18,14} - \beta_{18,13,14} - \beta_{16,13,14} - \beta_{17,13,14})$	methoxy	$\delta(CH_3)^{2}_{s}$
$S_{44} = (6^{-1/2})(2\beta_{17,16,14} - \beta_{16,18,14} - \beta_{17,18,14})$	methoxy	$\delta(CH_3)^{2'}_{as}$
$S_{45} = (2^{-1/2})(\beta_{16,18,14} - \beta_{17,18,14})$	methoxy	$\delta(CH_3)^{2''}_{as}$
$S_{46} = (6^{-1/2})(2\beta_{18,13,14} - \beta_{16,13,14} - \beta_{17,13,14})$	methoxy	$\gamma(CH_3)^{2'}_{as}$
$S_{47} = (2^{-1/2})(\beta_{16,13,14} - \beta_{17,13,14})$	methoxy	$\gamma(CH_3)^{2''}_{as}$
$S_{48} = (3^{-1/2})(\tau_{18,14,13,4} + \tau_{16,14,13,4} + \tau_{17,14,13,4})$	methoxy	*twist* $(CH_3)^2$

$r_{i,j}$ is the distance between atoms A_i and A_j; $\beta_{i,j,k}$ is the angle between vectors A_kA_i and A_kA_j; $\tau_{i,j,k,l}$ is the dihedral angle between the plane defined by A_i, A_j, A_k and the plane defined by A_j, A_k, A_l atoms; $\gamma_{i,j,k,l}$ is the angle between the vector A_kA_i and the plane defined by atoms A_j, A_k, A_l.

Table S4 Experimental wavenumbers $\tilde{\nu}$ (cm^{-1}), integral intensities I (relative) of the bands in the infrared spectrum of the photoproduct generated upon UV (λ>320 nm) irradiation of 4-methoxy-6-methyl-α-pyrone, compared with theoretical wavenumbers $\tilde{\nu}$ (cm^{-1}), absolute intensities Ath (km mol^{-1}) and potential energy distributions (%) calculated for 4-methoxy-6-methyl-1-oxa-2-oxobicyclo[2.2.0]hex-4-ene isomer **III**.

Experimental		Calculated		
Ar matrix		DFT(B3LYP)/6-311++G(d,p)		
$\tilde{\nu}$	I	$\tilde{\nu}$[a]	Ath	PED[b]
3033 3025	14	3166	3	$\nu(C5\text{-}H12)$ (99)
2982	41	3089	13	$\nu(CH_3)^{2'}_{as}$ (93)
2946	33	3059	9	$\nu(C3\text{-}H15)$ (99)
2911	5	3050	13	$\nu(CH_3)^{1''}_{as}$ (99)
2899	3	3038	12	$\nu(CH_3)^{1'}_{as}$ (98)
2871	2	3037	19	$\nu(CH_3)^{2''}_{as}$ (99)
2853 2849	7	2975 2968	13 41	$\nu(CH_3)^{1}_{s}$ (99) $\nu(CH_3)^{2}_{s}$ (92)
2840	3			
1909	15			
1873	20			
*1839 1828	501	1840	544	$\nu(C2{=}O7)$(88)
1787	13			
1645 *1632	318	1648	311	$\nu(C4{=}C5)$(70) + $\nu(C4\text{-}O13)$(19)
1462	25	1470	29	$\delta(CH_3)^{2'}_{as}$ (86)
1455	17	1467	12	$\delta(CH_3)^{2''}_{as}$ (90)
1442	7	1462 1454	4 4	$\delta(CH_3)^{1''}_{as}$ (85) $\delta(CH_3)^{1'}_{as}$ (61) + $\delta(CH_3)^{2}_{s}$ (25)
1435	3	1449	5	$\delta(CH_3)^{2}_{s}$ (69) + $\delta(CH_3)^{1'}_{as}$ (23)
1391	26	1391	18	$\delta(CH_3)^{1}_{s}$ (82) + $\nu(C6\text{-}C8)$(11)
1353	4	1332	3	$\nu(C6\text{-}C8)$(17) + $\nu(C5\text{-}C6)$(14) + $\delta(CH_3)^{1}_{s}$ (13) + $\nu(C3\text{-}C6)$(13)
1339	11			
*1303 1292 1282	240	1283	248	$\nu(C4\text{-}O13)$(20) + $\nu(C3\text{-}C4)$(19)
*1204 1193 1189	94	1189	50	$\gamma(CH_3)^{2'}_{as}$ (40)

1169	27	1178	27	γ(C3-H15)(48) + ν(C2-C3)(11)
1167		1169	28	δ(C5-H12)(17) + ν(O1-C2)(15)
1150	153	1149	128	δ(C5-H12)(15) + γ(CH$_3$)$^{2'}_{as}$ (14) + ν(O1-C2)(11) + γ(CH$_3$)$^{2''}_{as}$ (10)
1144		1145	25	γ(CH$_3$)$^{2''}_{as}$ (81)
1139		1136	19	γ(CH$_3$)$^{2'}_{as}$ (19) + δ(C5-H12)(18) + γ(CH$_3$)$^{1'}_{as}$ (14)
1070	3	1065	2	δ(C3-H15)(46) + ν(C6-C8)(13)
1026	98	1021	9	γ(CH$_3$)$^{1''}_{as}$ (31) + ν(O1-C2)(17)
1018		1013	62	ν(O13-C14)(48) + ν(C3-C4)(11)
*1010				
971	9	961	6	δ(C3-H15)(15) + δ ring 2 (13) + ν(C5-C6)(13) + ν(C2-C3)(10)
943	15	929	6	ν(C2-C3)(23) + γ(CH$_3$)$^{1'}_{as}$ (13) + ν(C5-C6)(12) + δ ring 2 (11)
937				
902	4	896	3	γ(CH$_3$)$^{1'}_{as}$ (20) + ν(C5-C6)(12) + ν(C3-C6)(11)
830	6	821	10	γ(C2=O7)(23) + ν(C3-C6)(13) + γ(C4-O13)(10) + γ(C5-H12)(10)
824				
817				
794	120	782	70	γ(C5-H12)(71)
782				
762	47	750	57	ν(O1-C2)(23) + ν(O1-C6)(21) + δ ring 1 (14) + δ(C2=O7)(15)
744	3			
724	7	702	20	ν(O1-C6)(23)
647	11	634	21	ν(O1-C6)(19) + δ ring 1 (19)
594	14	576	16	δ ring 2 (21) + ν(C6-C8)(20) + ν(C4-O13)(11) + ν(C3-C4)(10)
586				
556	3	535	9	γ(C4-O13)(45) + γ(C2=O7)(20)
		517	6	δ(O13-C14)(28) + δ(C4-O13)(23) + δ(C2=O7)(18)
		484	2	δ(C2=O7)(17) + τ butterfly (15) + δ(C6-C8)(11)
		394	10	τ butterfly (28) + ν(O1-C6)(16) + δ(C2=O7)(15)
		322	2	γ(C6-C8)(46)
		296	1	δ(C6-C8)(43) + δ(O13-C14)(24)
		213	0.1	*twist* (CH$_3$)^1 (93)
		183	1	δ(C6-C8)(28) + δ(C4-O13)(24) + δ(O13-C14)(21)
		164	1	*twist* (CH$_3$)^2 (44) + γ(C6-C8)(13) + τ ring 2 (12)
		128	3	τ ring 1 (43) + γ(C2=O7)(16) + γ(C6-C8)(13)
		107	2	*twist* (CH$_3$)^2 (36) + γ(C4-O13)(23) + τ ring 2 (18) + τ butterfly (10)
		58	5	τ(C4-OCH$_3$) (97)

[a] Theoretical positions of absorption bands were scaled by a factor of 0.98.

[b] PED's lower than 10% are not included. Definition of internal coordinates is given in Table S3.

Asterisks indicate the bands assigned to the rotamer **IV**.

Table S5 Calculated vibrational frequencies, intensities and potential energy distributions (PED) for 4-methoxy-6-methyl-1-oxa-2-oxobicyclo[2.2.0]hex-4-ene isomer **IV**; (wavenumbers ($\tilde{\nu}$) in cm^{-1}, theoretical intensities (A^{th}) in km mol^{-1}).

Calculated	DFT(B3LYP)/6-311++G(d, p)	
$\tilde{\nu}$ [a]	A^{th}	PED[b] (%)
3162	5	ν(C5-H12)(99)
3091	12	$\nu(CH_3)^{2''}_{as}$ (68) + $\nu(CH_3)^{2'}_{as}$ (24)
3067	7	ν(C3-H15)(100)
3050	14	$\nu(CH_3)^{1''}_{as}$ (99)
3037	12	$\nu(CH_3)^{1'}_{as}$ (98)
3029	25	$\nu(CH_3)^{2'}_{as}$ (75) + $\nu(CH_3)^{2''}_{as}$ (25)
2974	14	$\nu(CH_3)^{1}_{s}$ (99)
2964	38	$\nu(CH_3)^{2}_{s}$ (92)
1850	569	ν(C2=O7)(88)
1635	297	ν(C4=C5)(65) + ν(C4-O13)(23)
1469	11	$\delta(CH_3)^{2''}_{as}$ (68) + $\delta(CH_3)^{2'}_{as}$ (20)
1462	3	$\delta(CH_3)^{1''}_{as}$ (81)
1459	13	$\delta(CH_3)^{2'}_{as}$ (71) + $\delta(CH_3)^{2''}_{as}$ (22)
1453	4	$\delta(CH_3)^{1''}_{as}$ (78)
1437	13	$\delta(CH_3)^{2}_{s}$ (89)
1391	18	$\delta(CH_3)^{1}_{s}$ (83) + ν(C6-C8)(11)
1329	15	ν(C6-C8)(17) + ν(C3-C6)(14) + $\delta(CH_3)^{1}_{s}$ (11) + ν(C5-C6)(11)
1293	200	ν(C3-C4)(28) + ν(C4-O13)(13) + ν(C5-C6)(10)
1200	45	$\gamma(CH_3)^{2''}_{as}$ (46) + $\gamma(CH_3)^{2'}_{as}$ (15)
1181	7	γ(C3-H15)(56)
1161	87	ν(O1-C2)(24) + $\gamma(CH_3)^{1''}_{as}$ (11)
1148	28	$\gamma(CH_3)^{2''}_{as}$ (20) + $\gamma(CH_3)^{1'}_{as}$ (16) + ν(C3-C6)(11) + $\gamma(CH_3)^{2'}_{as}$ (10)
1147	10	$\gamma(CH_3)^{2'}_{as}$ (62)
1136	56	δ(C5-H12)(43) + $\gamma(CH_3)^{1''}_{as}$ (11)
1071	10	δ(C3-H15)(44) + ν(C6-C8)(12) + δ ring 2 (11)
1017	45	$\gamma(CH_3)^{1''}_{as}$ (27) + ν(O1-C2)(17)
1006	43	ν(O13-C14)(44) + ν(C3-C4)(17)
962	5	ν(O13-C14)(18) + δ(C3-H15)(17) + δ ring 2 (13) + ν(C5-C6)(13)
930	19	ν(C2-C3)(27)
899	17	$\gamma(CH_3)^{1'}_{as}$ (21) + ν(C5-C6)(19)
815	8	γ(C2=O7)(24) + ν(C3-C6)(16) + γ(C4-O13)(10)
775	119	γ(C5-H12)(62) + ν(O1-C6)(11)

759	31	ν(O1-C2)(20) + ν(O1-C6)(16) + δ(C2=O7)(11)
733	25	ν(O1-C6)(22)
674	7	δ ring 2 (20) + ν(O1-C6)(15) + δ ring 1 (11)
595	8	ν(C6-C8)(30) + δ ring 1 (15) + δ ring 2 (11)
556	10	γ(C4-O13)(45) + γ(C2=O7)(21)
488	4	δ(C2=O7)(28) + ν(C2-C3)(11) + τ butterfly (10)
451	2	δ(C4-O13) (22) + δ(O13-C14)(17) + ν(C3-C4)(16) + δ ring 2 (11)
421	5	τ butterfly (31) + δ(C2=O7)(16) + ν(O1-C6)(11)
334	3	γ(C6-C8)(40)
271	4	δ(C6-C8)(42) + δ(O13-C14)(18)
210	0.2	*twist* (CH_3)1 (89)
197	3	*twist* (CH_3)^2 (36) + τ ring 2 (15) + τ(C4-OCH_3)(13) + δ(C6-C8)(13)
181	3	δ(C4-O13)(33) + δ(O13-C14)(27) + γ(C6-C8)(10)
145	1	*twist* (CH_3)^2 (37) + τ(C4-OCH_3)(27) + τ ring 1 (12)
129	0.3	τ ring 1 (34) + γ(C6-C8)(19) + *twist* (CH_3)^2 (15) + τ ring 2 (15) + γ(C2=O7)(10)
84	4	τ(C4-OCH_3)(48) + γ(C4-O13)(20) + τ butterfly (12)

[a] Theoretical positions of absorption bands were scaled by a factor of 0.98.

[b] PED's lower than 10% are not included. Definition of internal coordinates is given in Table S3.

Table S6 Internal coordinates used in the normal mode analysis for the tautomer **VI** of 4-hydroxy-6-methyl-α-pyrone . (Atom numbering as in Scheme S1)

$S_1 = r_{1,2}$	ν(O1-C2)
$S_2 = r_{2,3}$	ν(C2-C3)
$S_3 = r_{3,4}$	ν(C3-C4)
$S_4 = r_{4,5}$	ν(C4-C5)
$S_5 = r_{5,6}$	ν(C5=C6)
$S_6 = r_{6,1}$	ν(O1-C6)
$S_7 = r_{7,2}$	ν(C2=O7)
$S_8 = r_{8,6}$	ν(C6-C8)
$S_9 = (3^{-1/2})(r_{9,8} + r_{10,8} + r_{11,8})$	$\nu(\mathrm{CH_3})^{1}{}_{s}$
$S_{10} = (6^{-1/2})(2r_{11,8} - r_{10,8} - r_{9,8})$	$\nu(\mathrm{CH_3})^{1'}{}_{as}$
$S_{11} = (2^{-1/2})(r_{10,8} - r_{9,8})$	$\nu(\mathrm{CH_3})^{1''}{}_{as}$
$S_{12} = r_{12,5}$	ν(C5-H12)
$S_{13} = r_{13,4}$	ν(C4=O13)
$S_{14} = (2^{-1/2})(r_{14,3} + r_{15,3})$	$\nu(\mathrm{CH_2})_s$
$S_{15} = (2^{-1/2})(r_{14,3} - r_{15,3})$	$\nu(\mathrm{CH_2})_{as}$
$S_{16} = (6^{-1/2})(\beta_{2,6,1} - \beta_{1,5,6} + \beta_{6,4,5} - \beta_{5,3,4} + \beta_{4,2,3} - \beta_{3,1,2})$	δ ring 1
$S_{17} = (12^{-1/2})(2\beta_{2,6,1} - \beta_{1,5,6} - \beta_{6,4,5} + 2\beta_{5,3,4} - \beta_{4,2,3} - \beta_{3,1,2})$	δ ring 2
$S_{18} = (1/2)(\beta_{1,5,6} - \beta_{6,4,5} + \beta_{4,2,3} - \beta_{3,1,2})$	δ ring 3
$S_{19} = (2^{-1/2})(\beta_{7,1,2} - \beta_{7,3,2})$	δ(C2=O7)
$S_{20} = (2^{-1/2})(\beta_{8,1,6} - \beta_{8,5,6})$	δ(C6-C8)
$S_{21} = (6^{-1/2})(\beta_{9,10,8} + \beta_{10,11,8} + \beta_{11,9,8} - \beta_{9,6,8} - \beta_{10,6,8} - \beta_{11,6,8})$	$\delta(\mathrm{CH_3})^{1}{}_{s}$
$S_{22} = (6^{-1/2})(2\beta_{9,10,8} - \beta_{10,11,8} - \beta_{11,9,8})$	$\delta(\mathrm{CH_3})^{1'}{}_{as}$
$S_{23} = (2^{-1/2})(\beta_{10,11,8} - \beta_{11,9,8})$	$\delta(\mathrm{CH_3})^{1''}{}_{as}$
$S_{24} = (6^{-1/2})(2\beta_{11,6,8} - \beta_{10,6,8} - \beta_{9,6,8})$	$\gamma(\mathrm{CH_3})^{1'}{}_{as}$
$S_{25} = (2^{-1/2})(\beta_{10,6,8} - \beta_{9,6,8})$	$\gamma(\mathrm{CH_3})^{1''}{}_{as}$
$S_{26} = (2^{-1/2})(\beta_{12,6,5} - \beta_{12,4,5})$	δ(C5-H12)
$S_{27} = (2^{-1/2})(\beta_{13,5,4} - \beta_{13,3,4})$	δ(C4=O13)
$S_{28} = \beta_{14,15,3}$	δ scissor ($\mathrm{CH_2}$)
$S_{29} = (1/2)(\beta_{14,2,3} - \beta_{15,2,3} + \beta_{14,4,3} - \beta_{15,4,3})$	δ rocking ($\mathrm{CH_2}$)
$S_{30} = (1/2)(\beta_{14,2,3} + \beta_{15,2,3} - \beta_{14,4,3} - \beta_{15,4,3})$	δ wagging ($\mathrm{CH_2}$)
$S_{31} = (1/2)(\beta_{14,2,3} - \beta_{15,2,3} - \beta_{14,4,3} + \beta_{15,4,3})$	δ twist ($\mathrm{CH_2}$)
$S_{32} = (6^{-1/2})(\tau_{6,1,2,3} - \tau_{1,2,3,4} + \tau_{2,3,4,5} - \tau_{3,4,5,6} + \tau_{4,5,6,1} - \tau_{5,6,1,2})$	γ ring 1

$S_{33} = (12^{-1/2})(2\tau_{6,1,2,3} - \tau_{1,2,3,4} - \tau_{2,3,4,5} + 2\tau_{3,4,5,6} - \tau_{4,5,6,1} - \tau_{5,6,1,2})$	γ ring 2
$S_{34} = (1/2)(\tau_{1,2,3,4} - \tau_{2,3,4,5} + \tau_{4,5,6,1} - \tau_{5,6,1,2})$	γ ring 3
$S_{35} = (6^{-1/2})(\tau_{11,8,6,5} + \tau_{11,8,6,1} + \tau_{10,8,6,5} + \tau_{10,8,6,1} + \tau_{9,8,6,5} + \tau_{9,8,6,1})$	*twist* (CH_3)[1]
$S_{36} = \gamma_{7,3,2,1}$	γ(C2=O7)
$S_{37} = \gamma_{8,1,6,5}$	γ(C6-C8)
$S_{38} = \gamma_{12,6,5,4}$	γ(C5-H12)
$S_{39} = \gamma_{13,5,4,3}$	γ(C4=O13)

$r_{i,j}$ is the distance between atoms A_i and A_j; $\beta_{i,j,k}$ is the angle between vectors A_kA_i and A_kA_j; $\tau_{i,j,k,l}$ is the dihedral angle between the plane defined by A_i, A_j, A_k and the plane defined by A_j, A_k, A_l atoms; $\gamma_{i,j,k,l}$ is the angle between the vector A_kA_i and the plane defined by atoms A_j, A_k, A_l.

Table S7 Experimental wavenumbers $\tilde{\nu}$ (cm^{-1}), integral intensities *I* (relative) of the infrared bands of 4-hydroxy-6-methyl-α-pyrone compared with theoretical^{a} wavenumbers $\tilde{\nu}$ (cm^{-1}), absolute intensities Ath (km mol^{-1}) and potential energy distributions (%) calculated for tautomers **V** and **VI**.

Experimental		Calculated^{a}			
Ar matrix		DFT(B3LYP)/6-311++G(d,p)			
$\tilde{\nu}^{b}$	I^{b}	form	$\tilde{\nu}^{c}$	Ath	PED^{d}
3614	124	**V**	3737	76	ν(O13-H14)(100)
3609					
3053	1	**V**	3163	1	ν(C5-H12)(99)
3018	7	**V**	3132	2	ν(C3-H15)(100)
2975	6	**V**	3069	10	$\nu(CH_3)^{1'}_{as}$ (97)
2936	7	**V**	3029	5	$\nu(CH_3)^{1''}_{as}$ (100)
2853	4	**V**	2976	9	$\nu(CH_3)^{1}_{s}$ (97)
1824					
1814	*96*	**VI**	1823	363	ν(C2=O7)(89)
1802					
1766	743	**V**	1776	751	ν(C2=O7)(81) + ν(C2-C3)(10)
1705	*87*	**VI**	1714	418	ν(C4=O13)(88)
1699					
1665	234	**V**	1650	229	ν(C5=C6)(45) + ν(C3=C4)(21)
1657	*31*	**VI**	1644	228	ν(C5=C6)(69)
1613	9				
1603					
1593					
1591	286	**V**	1576	298	ν(C3=C4)(39) + ν(C4-C5)(17) + ν(C5=C6)(16)
1589					
1527	4				
1497	8				
1472					
1469	64	**V**	1469	56	$\delta(CH_3)^{1'}_{as}$ (39) + ν(C4-C5)(13)
1441	*4*	**VI**	1449	18	$\delta(CH_3)^{1'}_{as}$ (85)
1434	10	**V**	1441	9	$\delta(CH_3)^{1''}_{as}$ (91)
1432	*2*	**VI**	1439	10	$\delta(CH_3)^{1''}_{as}$ (91)
1427	1	**V**	1436	2	$\delta(CH_3)^{1'}_{as}$ (48) + δ(C3-H15)(10)
1390		**VI**	1392	9	δ scissor (CH_2)(97)
1389	*18*	**VI**	1390	37	$\delta(CH_3)^{1}_{s}$ (87)
1387	4	**V**	1391	3	$\delta(CH_3)^{1}_{s}$ (91)
1380	1				

1361	1				
1350	1				
1340	*54*	**VI**	1329	211	ν(O1-C6)(19) + δ(C5-H12)(18) + ν(C4-C5)(17)
1285	9				
1270	*9*	**VI**	1271	27	δ wagging (CH_2)(71) + ν(C3-C4)(11)
1264	*17*	**VI**	1251	147	δ(C5-H12)(28) + ν(C4-C5)(15) + δ(C4=O13)(15)
1262 1253 1252 1249 1248	173	**V**	1247	176	ν(C4-O13)(28) + δ(C3-H15)(33)
1226	2				
1203 1199	70	**V**	1187	73	δ(O13-H14)(54) + δ(C3-H15)(13)
1189	5				
1167	*4*	**VI**	1157	13	ν(C6-C8)(32) + δ(C5-H12)(23) + ν(O1-C6)(10)
1162 1158	44	**V**	1154	63	δ(C5-H12)(39) + ν(C4-O13)(19)
1140	41	**V**	1114	53	ν(C2-C3)(32) + δ(C3-H15)(17) + ν(C8-C6)(11)
1128	28				
1120	*9*	**VI**	1076	156	ν(C2-C3)(26) + ν(O1-C2)(18) + ν(C4-C5)(10)
1111	2				
1099	3				
1042	6	**V**	1040	4	γ(CH_3)$^{1''}_{as}$ (78) + γ(C6-C8)(14)
1034	2	**VI**	1043	4	γ(CH_3)$^{1''}_{as}$ (76) + γ(C6-C8)(16)
1031 1030	20	**V**	1022	18	γ(CH_3)$^{1'}_{as}$ (57)
1024	*3*	**VI**	1019	11	γ(CH_3)$^{1'}_{as}$ (65)
991 *989*	*23*	**VI**	977	108	ν(O1-C6)(36) + δ ring 1 (23) + ν(O1-C2)(13)
987	170	**V**	975	63	ν(O1-C6)(38) + δ ring 1(21) + ν(C8-C6)(13)
983 980	78	**V**	972	3	ν(C4-C5)(34) + δ ring 1 (20) + ν(C3=C4)(10)
928	*8*	**VI**	932	20	δ rocking (CH_2)(50) + γ(C4=O13)(23) + γ(C2=O7)(17)
891	*7*	**VI**	876	9	ν(C3-C4)(34) + δ ring 1 (21) + ν(C4-C5)(19)
842	46	**V**	800	67	ν(O1-C2)(55) + δ ring 1 (15)
837	25	**V**	796	46	γ(C5-H12)(92) + γ(C4-O13)(15) + γ(C3-H15)(10)
821	*9*	**VI**	820	47	ν(O1-C2)(37) + ν(C2-C3)(19) + δ ring 1 (15)
814	71	**V**	791	32	γ(C3-H15)(77) + γ(C2=O7)(27) + γ(C5-H12)(10)
680	3	**V**	665	1	γ(C4-O13)(49) + γ ring 1 (32)
617	0.4	**V**	602	2	δ ring 1 (19) + ν(O1-C2)(15)

573	3	**V**	563	4	δ(C2=O7)(41) + δ(C4-O13)(17)
515	3	**V**	511	5	δ ring 3 (65) + ν(C8-C6)(10)
478	2				
441 434 428	94	**V**	439	109	τ(C4-OH)(97)

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[a] Tables with full IR spectra calculated for tautomers **V** and **VI** are given in Tables S8 and S9.

[b] Italized wavenumbers and intensities indicate bands assigned to form **VI.**

[c] Theoretical positions of absorption bands were scaled by a factor of 0.98.

[d] PED's lower than 10% are not included. Definition of internal coordinates is given in Tables S1 and S6.

Table S8 Calculated vibrational frequencies, intensities and potential energy distributions (PED) for 4-hydroxy-6-methyl-α-pyrone tautomer **V** (wavenumbers ($\tilde{\nu}$) in cm^{-1}, theoretical intensities (Ath) in km mol^{-1}).

Calculated DFT(B3LYP)/6-311++G(d, p)			
$\tilde{\nu}$ ^{a}	Ath	*Sym.*	PED^{b} (%)
3737	76	A’	ν(O13-H14)(100)
3163	1	A’	ν(C5-H12)(99)
3132	2	A’	ν(C3-H15)(100)
3069	10	A’	ν(CH$_3$)$^{1'}_{as}$ (97)
3029	5	A’’	ν(CH$_3$)$^{1''}_{as}$ (100)
2976	9	A’	ν(CH$_3$)$^{1}_{s}$ (97)
1776	751	A’	ν(C2=O7)(81) + ν(C2-C3)(10)
1650	229	A’	ν(C5=C6)(45) + ν(C3=C4)(21)
1576	298	A’	ν(C3=C4)(39) + ν(C4-C5)(17) + ν(C5=C6)(16)
1469	56	A’	δ(CH$_3$)$^{1'}_{as}$ (39) + ν(C4-C5)(13)
1441	9	A’’	δ(CH$_3$)$^{1''}_{as}$ (91)
1436	2	A’	δ(CH$_3$)$^{1'}_{as}$ (48) + δ(C3-H15)(10)
1391	3	A’	δ(CH$_3$)$^{1}_{s}$ (91)
1337	6	A’	δ(C5-H12)(26) + ν(O1-C6)(24) + ν(C2-C3)(10)
1247	176	A’	ν(C4-O13)(28) + δ(C3-H15)(33)
1187	73	A’	δ(O13-H14)(54) + δ(C3-H15)(13)
1154	63	A’	δ(C5-H12)(39) + ν(C4-O13)(19)
1114	53	A’	ν(C2-C3)(32) + δ(C3-H15)(17) + ν(C8-C6)(11)
1040	4	A’’	γ(CH$_3$)$^{1''}_{as}$ (78) + γ(C6-C8)(14)
1022	18	A’	γ(CH$_3$)$^{1'}_{as}$ (57)
975	63	A’	ν(O1-C6)(38) + δ ring 1(21) + ν(C8-C6)(13)
972	3	A’	ν(C4-C5)(34) + δ ring 1 (20) + ν(C3=C4)(10)
800	67	A’	ν(O1-C2)(55) + δ ring 1 (15)
796	46	A’’	γ(C5-H12)(92) + γ(C4-O13)(15) + γ(C3-H15)(10)
791	32	A’’	γ(C3-H15)(77) + γ(C2=O7)(27) + γ(C5-H12)(10)
702	0.001	A’’	γ ring 1 (27) + γ(C2=O7)(62) + γ(C3-H15)(15)
665	1	A’’	γ(C4-O13)(49) + γ ring 1 (32)
602	2	A’	δ ring 1 (19) + ν(O1-C2)(15)
563	4	A’	δ(C2=O7)(41) + δ(C4-O13)(17)
540	0.03	A’’	γ(C6-C8)(49) + γ(C4-O13)(20) + γ ring 3 (19)
511	5	A’	δ ring 3 (65) + ν(C8-C6)(10)
469	1	A’	δ ring 2 (79)

439	109	A’’	τ(C4-OH)(97)
355	13	A’	δ(C4-O13)(49) + δ(C2=O7)(24)
283	2	A’	δ(C6-C8)(66)
202	0.2	A’’	γ ring 2 (52) + γ ring 3 (25) + γ ring 1(10)
185	7	A’’	γ ring 3 (55) + *twist* (CH$_3$)^1 (23) + γ(C6-C8)(18)
148	0.06	A’’	γ ring 1(49) + *twist* (CH$_3$)^1 (21) + γ ring 2 (12) + γ(C6-C8)(12)
130	3	A’’	*twist* (CH$_3$)^1 (50) + γ ring 2 (37) + γ ring 3 (11)

[a] Theoretical positions of absorption bands were scaled by a factor of 0.98.

[b] PED’s lower than 10% are not included. Definition of internal coordinates is given in Table S1.

Table S9 Calculated vibrational frequencies, intensities and potential energy distributions (PED) for 4-hydroxy-6-methyl-α-pyrone tautomer **VI** (wavenumbers ($\tilde{\nu}$) in cm^{-1}, theoretical intensities (Ath) in km mol^{-1}).

Calculated	DFT(B3LYP)/6-311++G(d, p)	
$\tilde{\nu}$ ^{a}	Ath	PED^b (%)
3149	1	ν(C5-H12)(99)
3076	8	ν(CH$_3$)$^{1'}_{as}$ (96)
3063	0.1	ν(CH$_2$)$_{as}$ (69) + ν(CH$_2$)$_s$ (31)
3028	4	ν(CH$_3$)$^{1''}_{as}$ (100)
2976	4	ν(CH$_3$)^1_s (96)
2963	2	ν(CH$_2$)$_s$ (69) + ν(CH$_2$)$_{as}$ (31)
1823	363	ν(C2=O7)(89)
1714	418	ν(C4=O13)(88)
1644	228	ν(C5=C6)(69)
1449	18	δ(CH$_3$)$^{1'}_{as}$ (85)
1439	10	δ(CH$_3$)$^{1''}_{as}$ (91)
1392	9	δ scissor (CH$_2$)(97)
1390	37	δ(CH$_3$)^1_s (87)
1329	211	ν(O1-C6)(19) + δ(C5-H12)(18) + ν(C4-C5)(17)
1271	27	δ wagging (CH$_2$)(71) + ν(C3-C4)(11)
1251	147	δ(C5-H12)(28) + ν(C4-C5)(15) + δ(C4=O13)(15)
1175	6	δ twist (CH$_2$)(77)
1157	13	ν(C6-C8)(32) + δ(C5-H12)(23) + ν(O1-C6)(10)
1076	156	ν(C2-C3)(26) + ν(O1-C2)(18) + ν(C4-C5)(10)
1043	4	γ(CH$_3$)$^{1''}_{as}$ (76) + γ(C6-C8)(16)
1019	11	γ(CH$_3$)$^{1'}_{as}$ (65)
977	108	ν(O1-C6)(36) + δ ring 1 (23) + ν(O1-C2)(13)
932	20	δ rocking (CH$_2$)(50) + γ(C4=O13)(23) + γ(C2=O7)(17)
876	9	ν(C3-C4)(34) + δ ring 1 (21) + ν(C4-C5)(19)
824	16	γ(C5-H12)(95)
820	47	ν(O1-C2)(37) + ν(C2-C3)(19) + δ ring 1 (15)
617	3	γ(C2=O7)(33) + γ(C4=O13)(29)
599	1	ν(C3-C4)(13) + ν(O1-C6)(13) + δ ring 1 (10) + δ(C2=O7)(10)
569	1	δ(C2=O7)(31) + δ(C4=O13)(25)
556	1	γ(C6-C8)(42) + γ(C2=O7)(16)
514	4	δ ring 3 (33) + γ(C4=O13)(15) + δ rocking (CH$_2$)(12) + γ(C6-C8)(11)
462	5	δ ring 2 (59) + δ ring 3 (14)

432	11	δ ring 3 (26) + δ ring 2 (23) + δ rocking (CH_2)(14) + γ(C2=O7)(10)
381	9	δ(C4=O13)(32) + δ(C2=O7)(25) + ν(C3-C4)(15) + ν(C2-C3)(11)
289	1	δ(C6-C8)(68)
180	1	*twist* $(CH_3)^1$ (66) + γ ring 2 (11) + γ ring 3 (10)
146	2	γ ring 3 (30) + *twist* $(CH_3)^1$ (24) + γ ring 1 (23) + γ(C6-C8)(18)
119	4	γ ring 2 (87) + *twist* $(CH_3)^1$ (11)
72	12	γ ring 3 (51) + γ ring 1 (47)

[a] Theoretical positions of absorption bands were scaled by a factor of 0.98.

[b] PED's lower than 10% are not included. Definition of internal coordinates is given in Table S6.

Table S10 Experimental wavenumbers $\tilde{\nu}$ (cm^{-1}), integral intensities *I* (relative) of the bands in the infrared spectrum of the photoproduct generated upon UV (λ>320 nm) irradiation of 4-hydroxy-6-methyl-α-pyrone, compared with theoretical wavenumbers $\tilde{\nu}$ (cm^{-1}), absolute intensities Ath (km mol^{-1}) and potential energy distributions (%) calculated for 4-hydroxy-6-methyl-1-oxa-2-oxobicyclo[2.2.0]hex-4-ene isomer **VIII**.

Experimental		Calculated		
Ar matrix		DFT(B3LYP)/6-311++G(d,p)		
$\tilde{\nu}$	*I*	$\tilde{\nu}$ ^{a}	Ath	PED^{b}
3608	133	3726	82	ν(O13-H14)(100)
3603				
2999	15	3152	5	ν(C5-H12)(99)
2987				
2942	12	3067	7	ν(C3-H15)(100)
2894	2	3051	13	ν(CH$_3$)$^{1''}_{as}$ (99)
2872	4	3038	11	ν(CH$_3$)$^{1'}_{as}$ (98)
		2974	13	ν(CH$_3$)$^{1}_{s}$ (99)
1838	551	1853	567	ν(C2=O7)(88)
1640	261	1641	277	ν(C4=C5)(71) + ν(C4-O13)(19)
1634				
1454	5	1461	3	δ(CH$_3$)$^{1''}_{as}$ (83)
1440	3	1453	6	δ(CH$_3$)$^{1'}_{as}$ (81)
1393	23	1390	18	δ(CH$_3$)$^{1}_{s}$ (81) + ν(C6-C8)(11)
1383	24	1375	24	δ(O13-H14)(36) + ν(C3-C4)(23) + ν(C4-O13)(16)
1330	20	1323	27	ν(C6-C8)(20) + ν(C5-C6)(19) + δ(C5-H12) (15) + ν(C3-C6)(12) + δ(CH$_3$)$^{1}_{s}$ (12)
1315	3			
1199	59	1189	53	γ(C3-H15)(51) + δ(O13-H14)(14)
1185	14	1175	13	γ(CH$_3$)$^{1'}_{as}$ (16) + ν(O1-C2)(13) + γ(C3-H15)(12)
1183				
1166	32	1156	56	γ(CH$_3$)$^{1''}_{as}$ (19) + ν(C3-C6)(16) + ν(C5-C6)(12)
1147	95	1141	131	δ(C5-H12)(29) + ν(C4-O13)(17) + ν(O1-C2)(15) + γ(C3-H15)(11)
1132	8			
1112	99	1103	115	δ(O13-H14)(27) + δ(C5-H12)(22) + ν(C4=C5)(11)
1086	23	1063	11	δ(C3-H15)(44) + ν(C6-C8)(13)
1069	7			
1065				
1022	38	1014	41	γ(CH$_3$)$^{1''}_{as}$ (34) + ν(O1-C2)(21) + γ(CH$_3$)$^{1'}_{as}$ (12)
		971	2	ν(C3-C4)(22) + δ ring 2 (16) + δ(C3-H15) (14) + ν(C5-C6)(13)

944 941	24	933	14	ν(C2-C3)(33) + γ(C3-H15)(11) + ν(O1-C2) (10) + δ ring 1 (10)
911 905	3	902	5	ν(C5-C6)(26) + γ(CH$_3$)$^{1'}_{as}$ (25) + γ(CH$_3$)$^{1''}_{as}$ (10)
837	7	819	8	γ(C2=O7)(22) + ν(C3-C6)(16) + γ(C4-O13)(11)
825 819	3			
789	151	779	112	γ(C5-H12)(61)
770 765 761	25	757	44	ν(O1-C6)(31) + ν(O1-C2)(24) + δ ring 1 (10) + δ(C2=O7)(10)
729	4	715	10	ν(O1-C6)(16) + γ(C2=O7)(13) + ν(C2-C3)(11)
668	8	662	4	δ ring 1 (20) + δ ring 2 (19) + ν(C4-O13)(11)
597	11	586	8	ν(C6-C8)(30) + δ ring 2 (19)
546	5	550	3	γ(C4-O13)(46) + γ(C2=O7)(19)
499 495	8	488	15	δ(C2=O7)(27) + ν(C2-C3)(10)
450	3	440	4	δ(C4-O13)(31) + δ(C2=O7)(15) + τ butterfly (10)
408 404	28	423	85	τ(C4-OH)(73) + τ butterfly (11)
		376	48	δ(C4-O13)(22) + τ butterfly (19) + τ(C4-OH)(15)
		326	3	γ(C6-C8)(47)
		247	1	δ(C6-C8)(61) + δ(C4-O13)(14)
		213	0.04	*twist* (CH$_3$)^1 (93)
		142	1	τ ring 2 (40) + γ(C4-O13)(23) + γ(C6-C8)(21) + τ butterfly (10)
		133	2	τ ring 1 (47) + γ(C2=O7)(22) + τ butterfly (13)

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[a] Theoretical positions of absorption bands were scaled by a factor of 0.98.

[b] PED’s lower than 10% are not included. Definition of internal coordinates is given in Table S3.