SUPPORTING INFORMATION

Molecular and Electronic Structure of δ-Valerothiolactone

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Table S1. Crystal data and structure refinement for δ-valerothiolactone.

Empirical formula	C5 H8 O S
Formula weight	116.17 Da
Density (calculated)	1.347 g cm-3
F(000)	124
Temperature	188(2) K
Crystal size	0.3 mm diameter
Crystal color	yellow
Crystal description	cylindric
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\ \bar{1}$
Unit cell dimensions	a = 6.6573(1) Å α = 73.188(1)° b = 6.9608(1) Å β = 77.789(1)° c = 7.2829(1) Å γ = 62.946(1)°
Volume	286.447(7) Å^3
Z	2
Cell measurement reflections used	9935
Cell measurement theta min/max	3.37° to 27.50°
Diffractometer control software	Bruker AXS APEX 2 Vers. 2.0-2 2006
Diffractometer measurement device	Siemens SMART three axis goniometer with APEX II area detector system
Diffractometer measurement method	Data collection strategy APEX 2/COSMO chi + / - 10°
Theta range for data collection	3.37° to 27.52°
Completeness to theta = 29.46°	78.9 %
Index ranges	-8<=h<=8, -8<=k<=9, 0<=l<=7
Computing data reduction	Bruker AXS APEX 2 Vers. 2.0-2 2006
Absorption coefficient	0.438 mm^{-1}

Empirical absorption correction	Bruker AXS TWINABS Vers. 1.05
Max. / min. transmission	0.97 / 0.86
R(merg) before/after correction	0.0248 / 0.0204
Computing structure solution	Bruker AXS SHELXTL Vers. 6.12 W95/98/NT/2000/ME
Computing structure refinement	Bruker AXS SHELXTL Vers. 6.12 W95/98/NT/2000/ME
Refinement method	Full-matrix least-squares on F^2
Reflections collected	22265
Independent reflections	2035 [R(int) = 0.030]
Data / restraints / parameters	1909 / 0 / 65
Goodness-of-fit on F^2	1.024
Weighting details	$w = 1/[\sigma^2 (Fo^2)+ (0.0371*P)^2+0.0333*P]$ where $P = (Fo^2+2Fc^2)/3$
Final R indices [I>2sigma(I)]	$R1$ = 0.0238, $wR2$ = 0.0630
R indices (all data)	$R1$ = 0.0259, $wR2$ = 0.0644
Largest diff. peak and hole	0.305 and -0.128 eÅ^{-3}
Treatment of hydrogen atoms	Riding model on idealized geometries with the 1.2 fold isotropic displacement parameters of the equivalent Uij of the corresponding carbon atom
Comment	The crystallization was performed on the diffractometer at a temperature of 230 K with a miniature zone melting procedure using focused infrared-laser-radiation according to:R. Boese, .Nussbaumer,"In Situ crystallisation Techniques", in:"Organic Crystal Chemistry", Ed. D.W. Jones,Oxford University Press, Oxford,England, (1994) 20-37Data process details: Data reduction with two independent crystals after matrix determination with cell_now The low coverage resulted from the orientation of the cylindric crystal and the chosen scan mode, both due to the in situ crystal growing technique.Any other mounting of the crystal / scan mode would lead to a melting of the crystal.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) δ-valerothiolactone. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	3868(1)	3450(1)	7637(1)	32(1)
O(1)	4065(1)	7031(1)	7587(1)	40(1)
C(2)	6070(2)	743(1)	7358(2)	34(1)
C(3)	8316(2)	244(1)	7979(2)	33(1)
C(4)	9169(1)	1982(2)	6858(2)	32(1)
C(5)	7807(1)	4168(2)	7482(2)	30(1)
C(6)	5260(1)	5126(1)	7528(1)	26(1)

Table S3. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for δ-valerothiolactone. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
S(1)	25(1)	33(1)	40(1)	-6(1)	-6(1)	-14(1)
O(1)	38(1)	29(1)	50(1)	-12(1)	-4(1)	-10(1)
C(2)	41(1)	29(1)	36(1)	-6(1)	-7(1)	-17(1)
C(3)	33(1)	27(1)	32(1)	-5(1)	-6(1)	-7(1)
C(4)	24(1)	36(1)	31(1)	-8(1)	-1(1)	-10(1)
C(5)	28(1)	36(1)	32(1)	-9(1)	-3(1)	-17(1)
C(6)	29(1)	29(1)	19(1)	-5(1)	-2(1)	-13(1)

Table S4. Hydrogen coordinates (x 10^4) and i displacement parameters ($Å^2$ x 10^3) for δ-valerothiolactone.

	x	y	z	U(eq)
H(2A)	6293	692	6032	41
H(2B)	5569	-377	8072	41
H(3A)	9405	-1194	7797	40
H(3B)	8127	232	9316	40
H(4A)	9008	2249	5525	38
H(4B)	10743	1449	7004	38
H(5A)	8317	5250	6684	36
H(5B)	8164	3913	8758	36

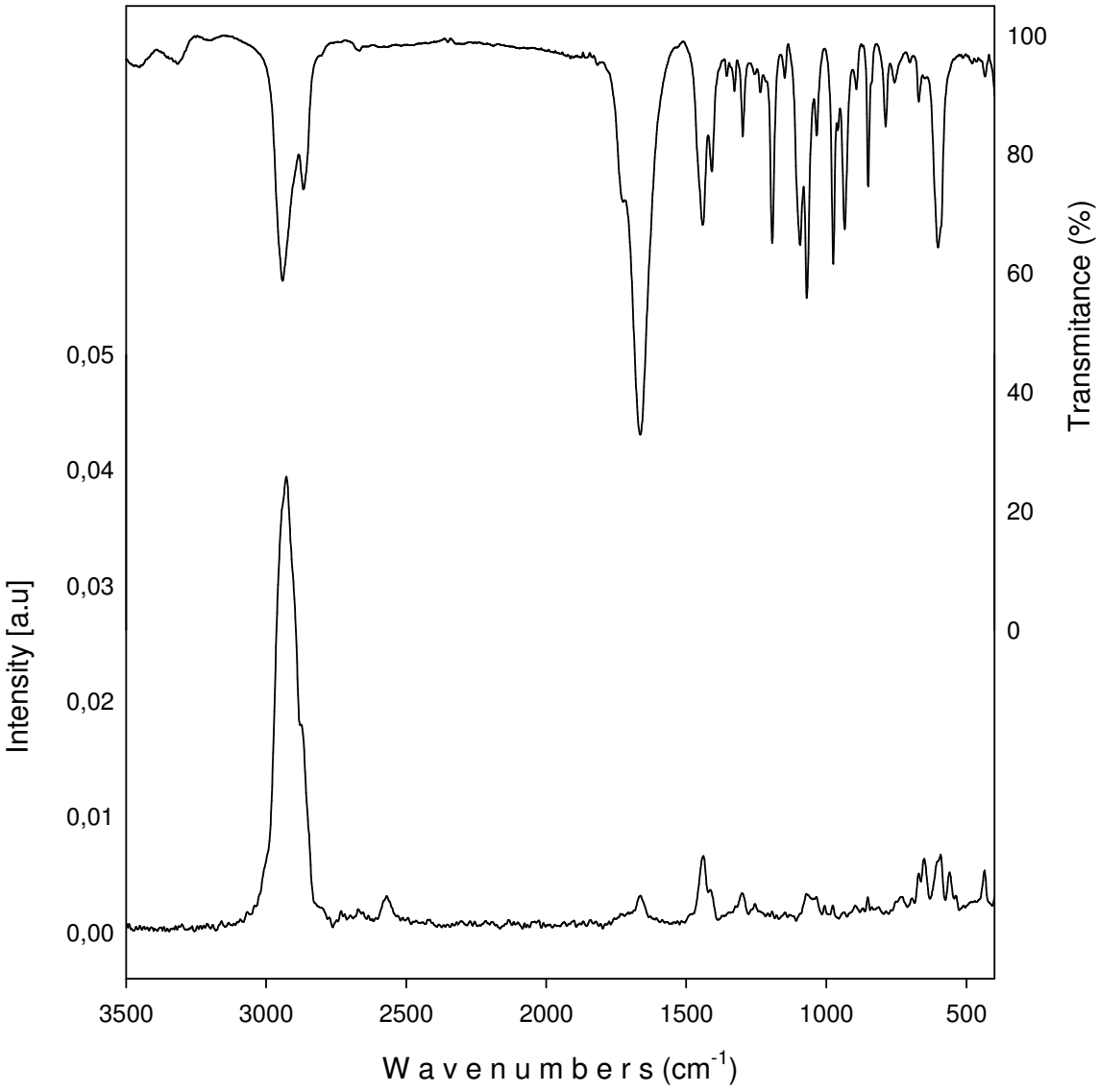
Table S5. Strain energies (kcal/mol) for δ-valerothiolactone determined using B3LYP and MP2 levels of approximation with the 6-311++G(d,p) basis sets.

	B3LYP	**MP2**
Isodesmic	-5.96	-13.68
Homodesmotic	5.06	6.02
Hyperhomodesmotic	4.85	7.54

Table S6. Mülliken Atomic charges for the molecular and cation radical form of *δ*-valerothiolactone calculated with UB3LYP/6-311++G(d,p) approximation.

	Atoms[(a)]								TAC[(b)]
	C2	C3	C4	C5	C6	S	O	H (av)	
$C_4H_8C(O)S$	-0.320	-0.338	-0.161	-0.303	-0.045	0.032	-0.231	0.170	0
$C_4H_8C(O)S^{\cdot+}$	-0.344	-0.396	-0.341	-0.300	0.053	0.487	-0.041	0.235	+1
$\Delta q^{(c)}$	-0.024	-0.058	-0.18	0.003	0.098	0.455	0.19	0.065	+1

[(a)] See figure 1 for atom numbering, [(b)] Total atomic charge, [(c)] $\Delta q = q(C_4H_8C(O)S.+) - q(C_4H_8C(O)S)$


Intensity [a.u]
0,05
0,04
0,03
0,02
0,01
0,00
100
80
60
40
20
0
Transmitance (%)
3500
3000
2500
2000
1500
1000
500
W a v e n u m b e r s (cm-1)