Supplementary Information

Towards a temperature guided molecular switch: An unusual reversible low temperature polymorphic phase transition in a conformationally locked environment

Goverdhan Mehta*[a] and Saikat Sen[a]

[a]Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012 INDIA

Contents

Experimental Section

1. General: Powder X-ray diffraction data was collected using CuK_α radiation on a Philips PANalytical X'Pert PRO MPD diffractometer, operating at 40 kV and 30 mA. The DSC data were recorded on a Mettler Toledo DSC823^e system.

2. X-Ray crystallography: Single crystal X-ray diffraction data was collected on a Bruker AXS SMART APEX CCD diffractometer. The X-ray generator was operated at 50 KV and 35 mA using MoK_α radiation. The data was collected with a ω scan width of 0.3°. A total of 606 frames per set were collected using SMART[1] in three different settings of φ (0°, 90° and 180°), keeping the sample to detector distance of 6.03 cm and the 2θ value fixed at -28°. The data were reduced by SAINTPLUS[1]; an empirical absorption correction was applied using the package SADABS[2] and XPREP[1] was used to determine the space group. The crystal structure was solved by direct methods using SIR92[3] and refined by full-matrix least-squares method using SHELXL97[4]. The geometric calculations were done by PARST[5] and PLATON[6]. For data collection at low temperature, a crystal of good quality and reasonable size (0.28×0.24×0.20 mm) was mounted in a Lindeman capillary and was cooled slowly from the ambient temperature to 100(2) K at a uniform rate of 40K/h with an Oxford Cryostream N_2 open-flow cryostat. A. The temperature of the crystal was then allowed to stabilize for 1 h; the unit-cell parameters were determined repeatedly every 15 min hereafter until the estimated standard deviations in cell dimensions did not vary beyond acceptable limits.

(a) Treatment of hydrogen atoms for diffraction data collected at 291 K: All hydrogen atoms were initially located in a difference Fourier map. The methine (CH) and methylene (CH_2) H atoms were then placed in geometrically idealized positions and allowed to ride on their parent atoms with C–H distances in the range 0.97–0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The CH_3 and OH hydrogen atoms were constrained to an ideal geometry with C–H distances as 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$, and O–H distances fixed at 0.82 Å and $U_{iso}(H) = 1.5U_{eq}(O)$. During refinement, each methyl and hydroxyl group was, however, allowed to rotate freely about its C–C or C–O bond respectively.

(b) Treatment of hydrogen atoms for diffraction data collected at 100 K: The positions of all H atoms were refined freely, along with an isotropic displacement parameter.


References:

(1)   Bruker. *SMART* (Version 6.028), *SAINT* (Version 6.02), *XPREP*. Bruker AXS Inc., Madison, Wisconsin, USA, 1998.

(2)   Sheldrick, G. M. *SADABS*. University of Göttingen, Germany, 1996.

(3)   Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Cryst.* **1994**, *27*, 435.

(4)   Sheldrick, G. M. *SHELXS97* and *SHELXL97*. University of Göttingen, Germany, 1997.

(5)   Nardelli, M. *J. Appl. Cryst.* **1995**, *28*, 659.

(6)   Spek, A. L. *J. Appl. Cryst.*, **2003**, *36*, 7.

Summary of crystal data, data collection, structure solution and refinement details

|	α form (291 K)	β form (291 K)	β form (100 K)
formula	$C_{18}H_{26}O_{10}$	$C_{18}H_{26}O_{10}$	$C_{18}H_{26}O_{10}$
M_r	402.39	402.39	402.39
crystal size [mm]	$0.32 \times 0.26 \times 0.24$	$0.22 \times 0.21 \times 0.12$	$0.28 \times 0.24 \times 0.20$
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	$C2/c$	$C2/c$	$C2/c$
a [Å]	21.433(7)	19.991(5)	19.430(4)
b [Å]	5.7126(18)	6.0024(15)	6.0815(13)
c [Å]	16.720(5)	16.225(4)	15.994(3)
α [°]	90	90	90
β [°]	105.664(5)	91.130(4)	91.849(4)
γ [°]	90	90	90
V [Å^3]	1971.1(11)	1946.5(8)	1888.9(7)
Z	4	4	4
F (000)	856	856	856
ρ_{calc} [g cm^{-3}]	1.356	1.373	1.415
μ [mm^{-1}]	0.111	0.113	0.116
reflns collected	6929	6976	7047
l.s. parameters	139	130	179
unique reflns	1800	1807	1853
observed reflns	1419	1475	1588
index range	$-25 \leq h \leq 25$	$-24 \leq h \leq 21$	$-23 \leq h \leq 22$
	$-6 \leq k \leq 6$	$-7 \leq k \leq 7$	$-7 \leq k \leq 7$
	$-20 \leq l \leq 20$	$-19 \leq l \leq 19$	$-19 \leq l \leq 19$
R_1 [$I > 2\sigma(I)$]	0.0514	0.0405	0.0343
wR_2 [$I > 2\sigma(I)$]	0.1402	0.1061	0.0796
goodness of fit (S)	1.052	1.049	1.034
$\Delta\rho_{max/min}$ [eÅ^{-3}]	0.213/-0.182	0.275/-0.188	0.376/-0.209

ORTEP plots of the α and β forms of the tetraacetate
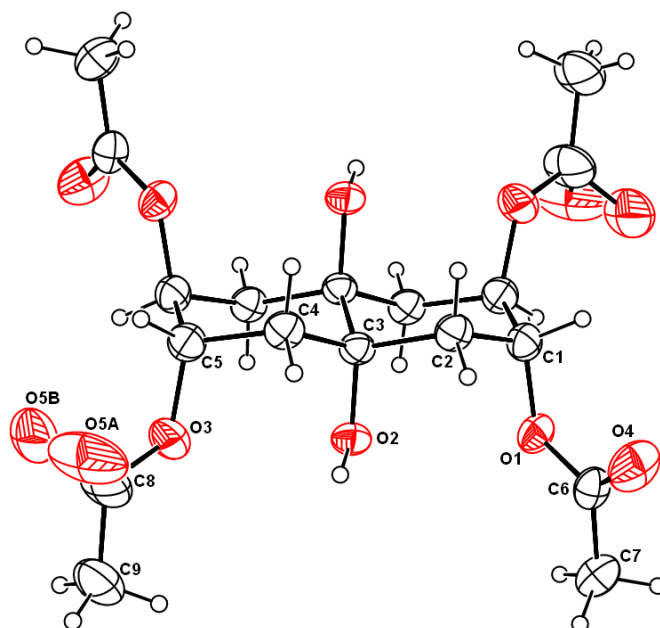
A view of the α form of the tetraacetate **1**, showing the atom numbering scheme. Displacement ellipsoids are drawn at 30% probability level and hydrogen atoms are shown as small spheres of arbitary radii.
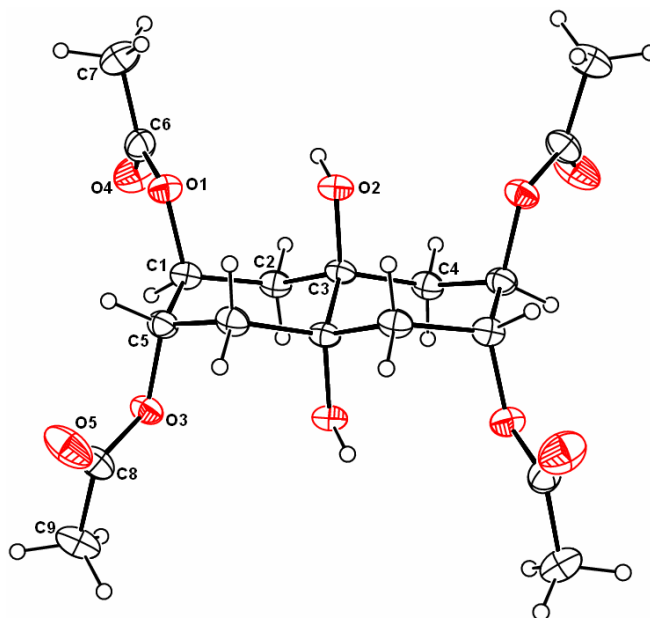

A view of the β form of the tetraacetate **1**, showing the atom numbering scheme. Displacement ellipsoids, as deduced from the data collected at 291 K, are drawn at 30% probability level and hydrogen atoms are shown as small spheres of arbitary radii.
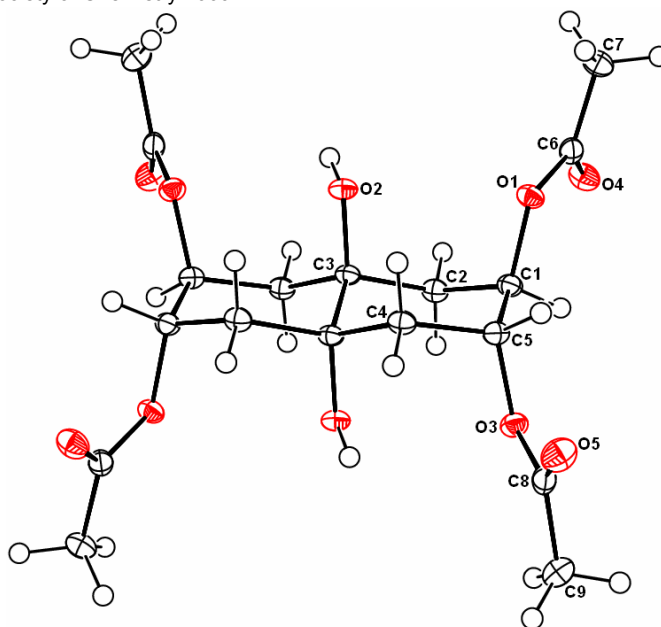
A view of the β form of the tetraacetate **1**, showing the atom numbering scheme. Displacement ellipsoids, as deduced from the data collected at 100 K, are drawn at 50% probability level and hydrogen atoms are shown as small spheres of arbitary radii.

PXRD patterns
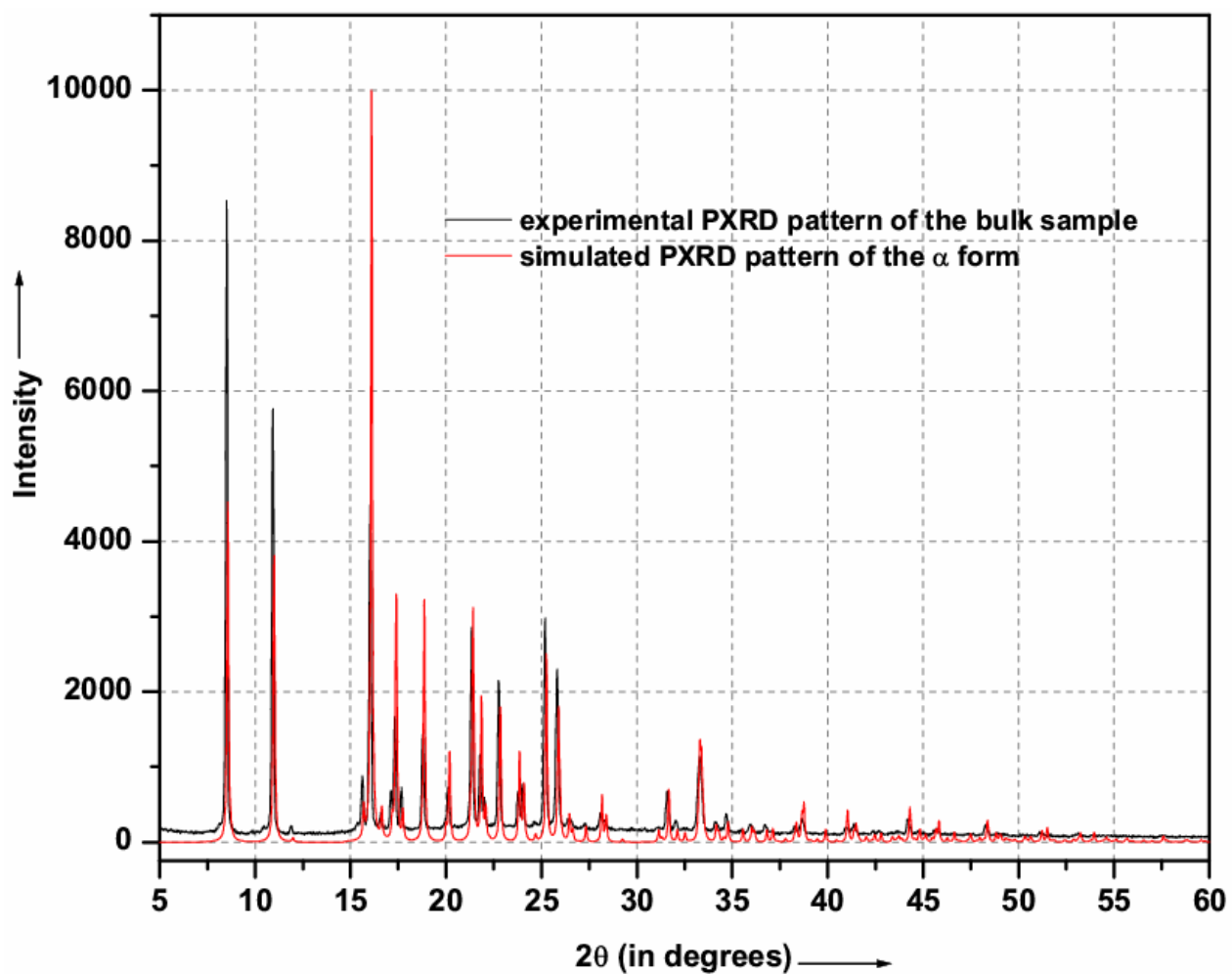
Comparison of the powder X-ray diffraction pattern recorded for a finely powdered bulk sample of the tetraacetate **1** with that simulated for the α form.
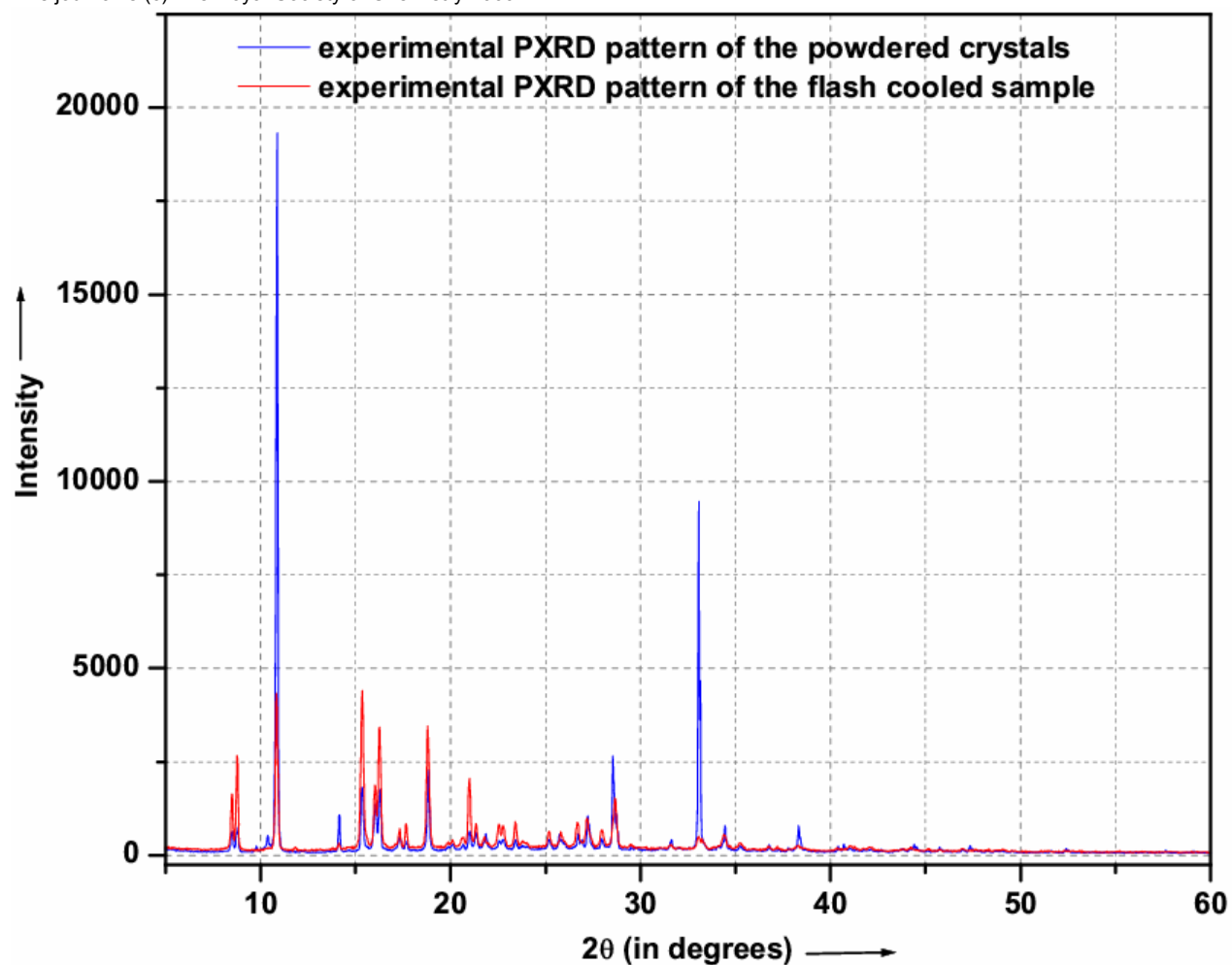
Comparison of the powder X-ray diffraction pattern recorded for the powder, obtained after flash cooling crystals of the α form of **1** at -78 °C, with that of a finely powdered sample of the tetraacetate crystals obtained through crystallization at -20 °C.