Mesomorphic properties of resorcinol

Mirosława D. Ossowska-Chruściel [a], Ewa Juszyńska-Gałązka [b], Wojciech Zając [b,*], Arkadiusz Rudzki [a], Janusz Chruściel [a]

[a] Siedlce University of Natural Sciences and Humanities, Institute of Chemistry, 3-go Maja 54, 08-110 Siedlce, Poland
[b] The Henryk Niewodniczański Institute of Nuclear Physics Polish Academy of Sciences, Radzikowskiego 152, 31-342 Kraków, Poland

HIGHLIGHTS

- There is no Crβ → Crα transition; Crystal α can only be obtained from melt or solution.
- The likely reason is the stabilizing role of tight H-bond network in solid phase.
- The role of H-bonds confirmed by vibrational spectra and DFT calculations.
- In DFT, 3-zeta basis with b-lyp functional performs better that 2-zeta with b3-lyp.
- The above makes a hint for resources-limited DFT calculations of like large systems.

GRAPHICAL ABSTRACT
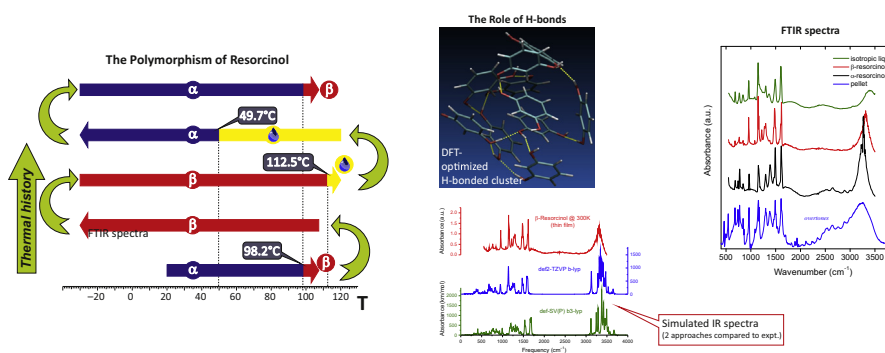
ABSTRACT

It is believed that hydrogen bonds to a great extent determine the polymorphism of resorcinol. In order to understand this more deeply, complementary studies of ambient pressure polymorphism of high-purity resorcinol were carried out by Differential Scanning Calorimetry (DSC), Polarizing Optical Microscopy (POM) and Transmitted Light Intensity (TLI), together with X-ray diffraction. Temperature-dependent infrared spectroscopy studies of this compound involved two-dimensional analysis. The present study delivers complex insight into the evolution of the vibrational spectra upon phase transitions, covering the whole range of frequencies. New results on thermal stability and the influence of thermal history upon the phase transitions are reported. The equilibrium geometries, vibrational frequencies, and infra-red intensities were additionally computed using the Density Functional Theory (DFT) with semi-empirical dispersion corrections, for hydrogen-bonded aggregates of resorcinol molecules.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Resorcinol is a well-known chemical, first studied in 19-th Century. Research performed to date includes structure analysis by means of both X-ray [1–3] and neutron [4–7] diffraction, vibrational spectroscopy [8–14], calorimetry [15], and molecular dynamics [17,18].

Resorcinol is also known as a component of various co-crystal systems, being under extensive study over the last decade. Two orientations of the this molecule in the hexamethylenetetramine-resorcinol co-crystal give rise to a modulated structure that undergoes an incommensurate/commensurate phase transition of the modulation vector [19]. Co-crystals of resorcinol and orcinol with

artemisinin are well known to the pharmaceutical industry [20]. Well known are also co-crystals of resorcinol and various simple heterocyclic compounds.

An extensive study of interconformational switching induced by hydrogen-bonded system of resorcinol [21, and references therein].

Resorcinol is now likely to regain the interest of researchers as it is an initial compound for the synthesis of many novel banana-shaped (bent-core) mesogens, resins and pharmaceuticals.

Four crystallographic forms of resorcinol have been found, commonly referred to as $\alpha, \beta, \gamma, \delta$. The forms α and β have been known since 1936–1938 [1–3]. The γ and δ forms are high-pressure-only phases [14]. The disordered γ phase appears at ca. 11 GPa, while δ phase develops at a rapid pressure increase to ca. 3 GPa. α-resorcinol undergoes transition into the β phase at ca. 96 °C with transition enthalpy of 1.37 kJ mol^{-1} [15]. Previous papers reported the $\alpha \rightarrow \beta$ transition at 75 °C [1,3]; the difference is attributed to the sample purity. The purer the material the higher the transition temperature. The melting point was found around 110 °C with transition enthalpy of 54.59 kJ mol^{-1}. The $\alpha \rightarrow \beta$ transition can also be induced by applying external pressure of ca. 0.5 GPa [11,12].

The α and β forms of resorcinol differ not only with respect to the crystal structure parameters but also with respect to molecular conformation [15], as shown in Table 1. The presence of two hydroxyl groups located at the 1 and 3 positions of the benzene ring means there are three conformational isomers possible. Ground state SCF (Self-Consistent Field) energies of an isolated resorcinol molecule have been calculated for each conformer, using DFT at a high level of theory, namely: "quadruple-zeta" basis set (def2-QZVPPD) and B3-LYP functional with semi-empirical dispersion corrections (Grimme) [22], as implemented in Turbomole [23], with tight SCF convergence criterion, set to 10^{-9} Ha (see Table 1). Two hydroxyl groups per a relatively small molecule mean that a tight network of hydrogen bonds will to a great extent influence not only the structure of solid forms of resorcinol but also the phase transitions between them.

The "up–up" and "up–down" conformers have relatively close ground state SCF energies, hence it is easy for resorcinol to change its conformation upon the $\alpha \rightarrow \beta$ transition. Such a situation is by no means a surprise. A few almost equienergetic conformations of orcinol lead to a wealth of crystal and co-crystal structures formed by networks of hydrogen-bonded molecules of this compound [16]. This qualitative observation should be, however, taken with care. Hydrogen-bonded co-crystal systems involving resorcinol on one hand and orcinol on another, show many dissimilarities,

possibly caused by different networks of hydrogen bonds. This was mentioned in [20], and concluded as a striking effect in [16] (orcinol–urea vs. resorcinol–urea co-crystals).

Despite extensive research carried out on resorcinol, thermal stability of its solid phases has not been determined, neither the influence of thermal history or cooling/heating rates upon transition temperatures studied.

2. Experimental and computation methods

2.1. DSC, POM and TLI measurements

Commercial resorcinol was repeatedly crystallized from benzene many times. The chemical purity was checked by thin layer chromatography (TLC) and further confirmed by elemental analysis using Perkin–Elmer 2400 spectrometer. The phase transition temperatures were determined by means of differential scanning calorimety (DSC), with DSC 822^e Mettler Toledo Star System, by polarized optical microscopy (POM) and transmitted light intensity (TLI) measurements (see [24] for description of the set-up). Heating and cooling rates for all DSC, TLI and POM measurements were the same: 2.0 K min^{-1}, and 0.1, 5.0 and 10 K min^{-1} for additional DSC scans, with the precision of 0.1 K (Linkam controller). TLI and POM measurements were done on planar samples, using AWAT electro-optic HG-type cells, 6.4 µm thick with ITO electrodes. Linkam programmable heating and cooling stage THMSE 600 was used.

2.2. FT-IR

IR spectra were recorded on two instruments independently. The first was Fourier Transform Middle-Infrared (FT-MIR) Nicolet Magna 760 spectrometer equipped with the KS20 temperature controller from Chino. A minimum of 64 co-added scans were recorded. The spectra were taken in the range of 400–4000 cm^{-1} at the resolution of 1 cm^{-1}. The samples 5.6 µm thick were sandwiched between two ZnSe windows, transparent to infrared radiation. The second series of infrared (IR) absorption measurements over the same frequency range spectra were performed with the EXCALIBUR FTS-3000 spectrometer, on pelleted samples of resorcinol mixed with KBr. During the experiments, the spectrometer was purged with dry nitrogen. The transmission spectra were measured with a resolution of 4 cm^{-1} and taking 64 scans. Infrared spectra were collected in the crystal phases of resorcinol up to the liquid phase, cycling through heating and cooling, thereby providing experimental conditions suitable for taking into account thermal history of the sample.
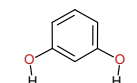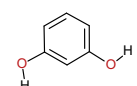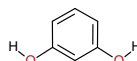
2.3. X-ray diffraction

XRD studies were carried out on X'Pert PRO (PANalytical) diffractometer using the Cu Kα radiation ($\lambda = 1.50589$ Å) and a graphite monochromator. The instrument is capable of maintaining angular positioning precision of about 0.001. The sample temperature was stabilized with the accuracy of ±0.1 K using a continuous flow cryostat supplied by Anton Paar Co. The sample was placed in a nickel-plated copper sample holder of dimensions $18 \times 9 \times 0.2$ mm. Diffraction patterns were recorded each 5 °C in the temperature range -188 °C $< T < 102$ °C during cooling and heating. After each temperature change the sample was allowed to equilibrate for 10 min.

Additional X-ray diffraction measurements were performed on Guinier symmetrical focusing transmission photographic camera.

Table 1
Resorcinol conformers and corresponding ground state SCF energies of isolated molecules.

Conformer	SCF Energy (Ha (hartee))
"up–up", **crystal form** α	−382.6857372
"up–down", **crystal form** β	−382.6857823
"down–down"	−382.6846866