

The structural phase transition in deuterated benzil, $C_{14}D_{10}O_2$

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The first order structural phase transition of benzil, from a $P3_121$ phase above ~ 85 K to a monoclinic $P2_1$ phase below, has been re-examined using capacitance measurements, neutron powder diffraction, and neutron inelastic scattering. The isotope effect is shown to be the result of the increase in mass of the phenyl groups on deuteration. Models from the literature of the phase transition suggest that a zone-centre phonon softening triggers the condensation of a Bragg peak at the M -point ($0 \frac{1}{2} 0$) on the Brillouin zone boundary. This is explored using neutron inelastic scattering, which suggests that the triggering is unlikely.

1. Introduction

Figure 1 shows a molecule of benzil, $C_{14}H_{10}O_2$. At 300 K benzil occurs in space group $P3_121$ ($a = 8.402 \text{ \AA}$, $c = 13.655 \text{ \AA}$ (hexagonal setting) [1]. Isostructural with α -quartz, it has been called ‘organic quartz’ [2]. On cooling benzil undergoes a phase transition to a ferroelectric ferroelastic phase, $T_c = 83.5 \text{ K}$ [3-5]. The low temperature phase is of space group $P2_1$

($a = 14.380 \text{ \AA}$, $b = 8.373 \text{ \AA}$, $c = 13.359 \text{ \AA}$ and $\beta = 88.82^\circ$ at 70 K [1]). Bulk measurements (e.g. Raman [3]) show that a mode of E -symmetry softens as the phase transition is approached from above; but the cell doubling at the transition requires softening at the zone boundary (at the M -point, $(0 \frac{1}{2} 0)$) while these measurements apply to Γ , the Brillouin zone centre. Hence it has been suggested that the cell doubling is due a softening at the zone boundary triggered by a non-linear interaction

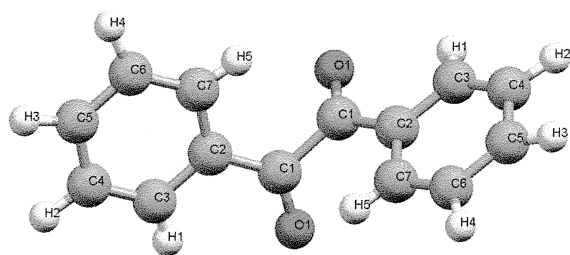


Figure 1: Schematic diagram of a molecule of benzil, showing H (D) atoms (white), C (grey) and O (red).

between Γ -point and an M -point order parameters [4]. The behaviour of the modes at M has never been observed directly; that is done here using neutron inelastic scattering (NIS). First it must be shown that hydrogenous benzil, h-benzil, and deuterated benzil, d-benzil, behave the same at the phase transition (d-benzil must be used for the neutron measurement). To this end capacitance measurements and neutron powder diffraction were performed.

2. Experimental

Crystals ($5 \times 5 \times 5 \text{ mm}^3$) of h- and d-benzil were grown by controlled evaporation of solvent from a seeded, saturated acetone solution. They were used to obtain T_c in h- and d-benzil using a capacitance bridge dilatometer in which the sample acted as dielectric in a capacitor. Neutron powder diffraction (NPD) was performed using the MRPD at the Bragg

Institute; as-purchased d-benzil was crushed into fine powder, loaded into a vanadium can and attached to a closed cycle helium refrigerator. A single crystal of d-benzil of size $16 \times 8 \times 6 \text{ mm}^3$ was used in the NIS measurements, carried out at HFIR, Oak Ridge National Laboratory, using the HB1 triple axis spectrometer. The long axis was the hexagonal c -axis, which was aligned vertically inside a sealed sample can attached to the copper block of a closed cycle refrigerator such that the horizontal scattering plane of the HB1 TAS allowed measurements at wavevectors in the a^*b^* plane in reciprocal space to be performed.

3. Results

3.1 Dielectric Measurements

T_c for h-benzil from capacitance measurements agreed with the published figure. T_c for d-benzil was $88.1 \pm 0.5 \text{ K}$ (Fig. 2), an increase of 5.5%. Small, and explicable through the fractional increase in mass of the phenyl ring upon deuteration.

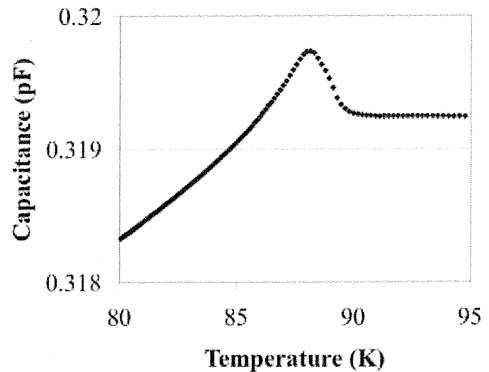


Figure 2: Capacitance versus T for d-benzil. Crystal orientation arbitrary.

3.2 Neutron Powder Diffraction

Fig. 3 shows a pattern for d-benzil at 15K, fitted by the $P2_1$ spacegroup, showing that d-benzil goes into the same phase as h-benzil below T_c [5]. Similar fits showed that above T_c the structure was indeed the expected $P3_121$ cell. Hence there is no evidence that the structures found in d-benzil differ from those in h-benzil. To test that the phase transition remained first order, data was collected as a function of T for temperatures between 10 and 150K. Plots of a , b , c and volume per benzil molecule against T showed little systematic behaviour.

However, extrapolation of β against T suggested $T_c = 98 \text{ K}$, while capacitance measurements showed it to be near 88K. Further, the pattern collected at 89K showed coexistence of the phases. This suggests that the structural transition in d-benzil is of first order, as it in h-benzil [6].

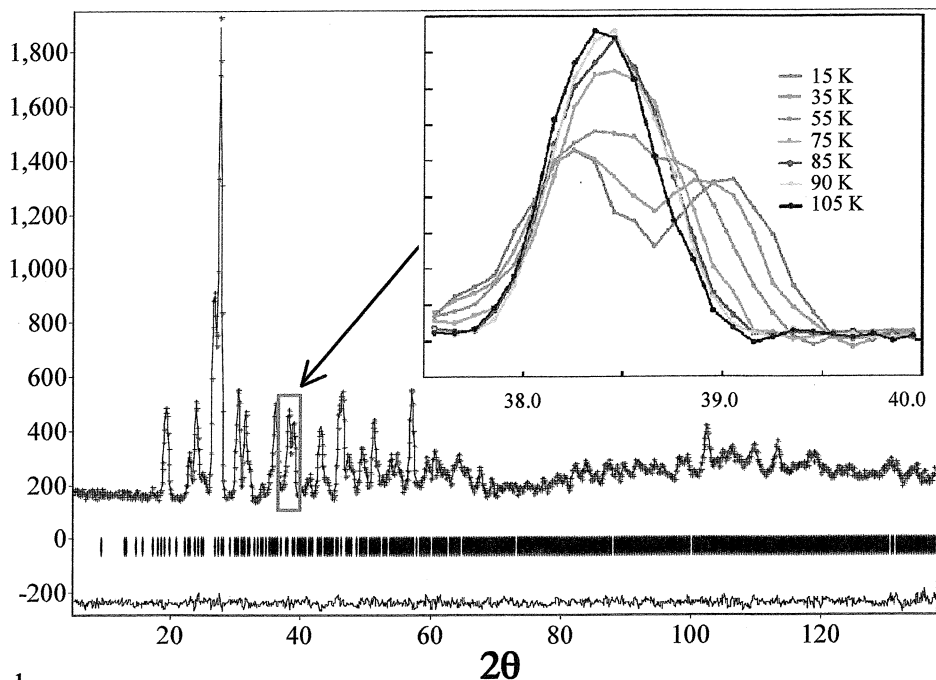


Figure 3: NPD pattern of d-benzil at 15K, fitted in $P2_1$. Upper line is fit to data, vertical bars denote Bragg positions and lower line is difference plot. Inset: peak at $37.5\text{-}40^\circ$ as it evolves with T .

3.3 Neutron Inelastic Scattering

Using NIS it was possible to examine the T dependence of the lowest energy phonon modes at the M -point on the Brillouin zone boundary. This could be compared with the T dependence of the zone-centre mode thought to trigger the; phase transition (' E mode' [4]) by looking at results from the literature (Fig. 4). This shows the TA mode at M softening faster both relatively and in absolute terms than the zone centre mode, suggesting that the zone centre mode is not triggering the phase transition but that it is a conventional soft mode phase transition.

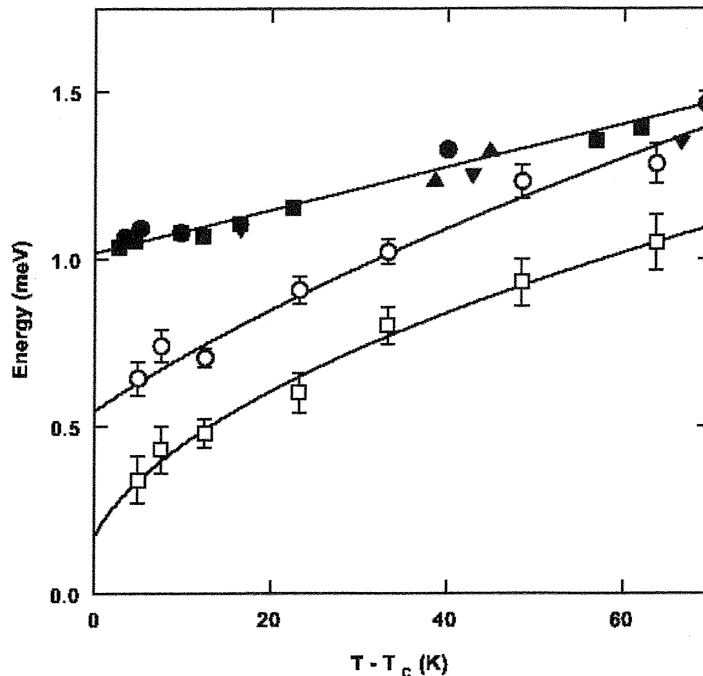


Figure 4: T dependence of phonon energy (○) and critical energy width (□) for TA mode at the M -point plotted on the same scale as results for the suggested triggering mode (E mode) at Γ from the literature. ● is from [3], ■ from [7], ▲ from [8] and ▼ from [9].

Conclusions

Deuteration modifies the behaviour of benzil only slightly, unlike some other ferroelectrics, and the phase transition appears to be a conventional soft mode transition, which does not require the invocation of order parameter coupling to explain the unit cell doubling.

Acknowledgments

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References

- [1] M.More, G.Oudou and J.Lefebvre, *Acta Cryst.* **B43** (1987) 398
- [2] R.Claus, H.H.Hacker, H.W.Schrötter, J.Brandmüller and S.Haussühl, *Phys. Rev.* **187** (1969) 1128
- [3] D.R.Moore, V.J.Tekippe, A.K.Ramdas, and J.C.Tolédano, *Phys. Rev. B* **23** (1983) 7676
- [4] J.C.Tolédano, *Phys. Rev B*, **20** (1979) 1147
- [5] B.Hunter, *IUCr Commission on Powder Diffraction Newsletter No. 20* (1998)
- [6] D.J.Goossens, Xiaodong Wu and M.Prior, *Solid State Commun.* **136** (2005) 543
- [7] J.Sapriel, A.Boudou, and A.Perigaud, *Phys. Rev. B* **19** (1979) 1484
- [8] J.Petzelt, Y.G.Goncharov, G.V.Kozlov, A.A.Volkov, B.Wyncke, and F.Brehat, *Czech. J. Phys.* **B34** (1984) 887
- [9] M.A.Ivanov, V.A.Kimasov, and Y.F.Markov, *Physics of the Solid State* **44** (2002) 373