High Pressure Studies of Tetrachloro-o-benzoquinone by NQR Spectroscopy*

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Tetrachloro-o-benzoquione (TOB) crystallizes in two different forms. The two forms, Sample I and Sample II, show different phases and NQR spectra. When subjected to pressures higher than about 40 MPa the α phase is converted to the γ phase. X-ray powder patterns studies as well as DTA measurements have confirmed this result. Heating the γ phase above 310 K reverses this process.

1. Introduction

Benzoquinones belong to one of the most representative classes of molecules acting as π-electron acceptor in the so called "molecular addition compounds" [1]. In the work of Jugie et al. [2], who studied tetrachloro-o-benzoquinone (TOB), it was shown that, depending on the procedure which is used for purifying of TOB, one gets two different forms of this compound with different structure and NQR spectrum. Sample I was obtained by sublimation of the commercial product and Sample II by very slow crystallization at low temperature (250 K) from an ether solution, the solvent of which was allowed to evaporate in a slow stream of dry nitrogen [2].

The samples show different NQR spectra. Sample I exhibits a phase transition at 213 K. In the high temperature phase (α-TOB) it shows two NQR lines while below the phase transition temperature (β-TOB) it shows four lines. Sample II exhibits a phase transition at 210 K. In the high temperature phase (γ-TOB) it shows four lines while in the low temperature phase (δ-TOB) it shows 16 lines [2].

Additionally, as was shown in [2], the γ phase, when heated over 305 K, changes into the α phase.

In order to obtain more information about the nature of the phase transitions in TOB, high pressure NQR studies have been performed.

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2. Experiments

The ^{35}Cl NQR frequency measurements were carried out with an ISSh 1-12 type, incoherent, pulse spectrometer equipped with an automatic frequency sweep. The $\pi/2-\tau-\pi$ sequence for spin echo was applied, with typical pulse widths of 15 μs and 30 μs. The gate in the boxcar integrator was opened for one μs after 2τ time, thus recording the amplitude of the echo signal as a function of frequency.

The pressures were generated by means of a Unipress, three-stage, helium-gas compressor. The pressure cell was made of beryllium-copper alloy and heat treated to a Rockwell hardness of C-39 to C-41. Details of our pressure device are described in [3]. The pressure vessel was suspended in a cryostat and nitrogen was used as a cryogenic fluid.

DTA was performed by use of a homemade apparatus already described [4].

The X-ray powder patterns were recorded at room temperature with a model VD-1A diffractometer from Shimadzu Co., equipped with a copper anticathode.

3. Results and Discussion

NQR

The observd NQR spectra of both TOB forms were in full agreement with the results presented by Jugie et al. [2]. Figure 1 shows the NQR spectra of the lower temperature phase (77 K) of both forms of TOB. The four lines of Sample I are shown in Figure 1 A. The spectrum of Sample II is shown in Figure 1 B. Due to poor resolution it was impossible to recognize all sixteen lines. For this reason the pressure experiments

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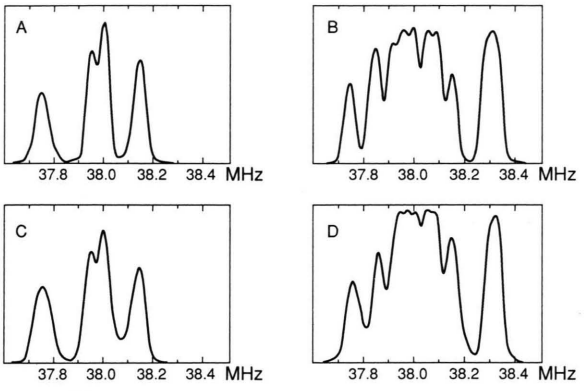

Fig. 1. ^{35}Cl NQR spectra of TOB in different forms (at 77 K): A) Spectrum of Sample I. B) Spectrum of Sample II. C) Spectrum of Sample I′ after heating to over 310 K. D) Spectrum of Sample I′ (Sample I after applying pressure of 150 MPa).

were mainly carried out with Sample I. However, these high pressure NQR studies have shown that Sample I, after being subjected to pressures higher than 40 MPa, changes into another form which we will designate as Sample I′. After repeating this experiment several times it became clear that this "new" form has an NQR spectrum very similar to that of Sample II. Figure 1 D presents the NQR spectrum (at 77 K) obtained for Sample I after applying high pressure. As one may see, it shows a remarkable resemblance to the NQR spectrum of Sample II (Figure 1 B). This would suggest that high pressure changes the α phase of Sample I into the γ phase of Sample II. After heating Sample I′ to temperatures over 310 K one obtains a spectrum which is characteristic of Sample I (Figure 1 C). Such behavior is typical for Sample II in which the γ phase has been shown to change into the α phase of Sample I with heating [2].

However, the poor resolution of the NQR lines obtained for Sample II as well as for Sample I′ does not allow for stating with absolute confidence that these spectra are identical.

X-ray Powder Patterns and DTA

In order to confirm the assumption that high pressure changes the α phase of Sample I into the γ phase of Sample II, X-ray powder patters as well as DTA measurements were performed for both samples.

As it was shown by Jugie et al. [2], the Samples I and II have different structures. Sample I crystallizes with the space group P2/a while Sample II with the space group $P2_2/c$.

X-ray powder patterns have been recorded for both forms of TOB (Sample I′ and Sample I′ after heating to over 310 K). The patterns of Sample I′ were the same as for Sample II while the patterns of the heated Sample I′ were once more the same as those of Sample I.

The DTA measurements confirm that Sample I and Sample II differ in the temperatures of their phase transitions. Additionally, Sample II exhibits a phase transition at about 310 K in which this form of TOB changes into form of Sample I. This heat anomaly, connected with the transition at 310 K, was observed for Sample II and Sample I′ and was not observed in Sample I nor in either of the heated samples.

All these measurements confirm the earlier assumptions. In the case of TOB crystals, high temperature and pressure act in opposite ways: heating changes the γ phase of TOB (Sample II) into the α phase (Sample I) while high pressure changes the α phase into the γ phase. The cycle of pressure – high temperature – pressure – ... has been repeated several times for one sample giving as a result the NQR spectra characteristic for Sample II – Sample I – Sample II –..., respectively.

A general comparison of bond lengths and bond angles shows a remarkable identity between both forms of TOB [2]. Drastic differences occur when the packing of both forms is to be compared. It seems that in the described transitions of one form of TOB into another the volume of the crystal plays an essential role. When Sample II is being heated, its volume increases, thus allowing for the changes in the packing of the molecules in the crystal. The pressure, by decreasing the crystal volume, forces the opposite change. Further studies are needed for a better understanding of the observed phenomena.

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