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Published version information

This is the peer reviewed version of the following article:

Citation: Wolf H, Lock N, Parker SF and Stalke D. "Direct spectroscopic evidence of the mechanism behind the phase transition of [2,2]-paracyclophane." *Chemistry – A European Journal*, vol. 21, no. 12 (2015): 4556–4560.

which has been published in final form at [10.1002/chem.201405948](https://doi.org/10.1002/chem.201405948). This article may be used for non-commercial purposes in accordance With Wiley-VCH Terms and Conditions for self-archiving.

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Cyclophane Phase Transition

Direct Spectroscopic Evidence of the Mechanism behind the Phase Transition of [2,2]-Paracyclophane

Hilke Wolf,^[a] Nina Lock,^[a,b] Stewart F. Parker^[c] and Dietmar Stalke^{*[a]}

Abstract: [2,2]-paracyclophane undergoes phase transitions at 45 K and 60 K. Based on simultaneous Raman spectroscopy and inelastic neutron scattering experiments (12–70 K) it is shown that a twisting motion of the ethylene bridge perpendicular to the plane of the aromatic rings drives the phase transition. The low temperature (< 45 K) and high temperature (> 60 K) conformers only differ by this twisting motion which freezes out below 45 K and is thermally averaged above 60 K. Between 45 and 60 K the system gains energy until the phase transition is complete.

Non-destructive phase transitions are very rarely observed in single crystals as a change in conformation often also triggers a change in the crystal packing. This often leads to the destruction of the single crystal and both phases have to be studied separately. [2,2]-Paracyclophane (paracyclophane) is an exception and undergoes a non-destructive phase transition, the crystals even support repeated cooling and heating, thus the structure has been studied at variable temperatures using single crystal X-ray diffraction. Nevertheless, till very recently there was a dispute in the literature on the structure of this small molecule. Paracyclophane is a member of the cyclophane family which is very well studied and has been the focus of both theoretical and experimental research for almost 70 years. After its discovery in 1949 as a side product in a polymerization reaction^[1] it has shown great versatility in both inorganic and organic chemistry. Paracyclophane and its higher homologues readily undergo Diels-

Alder reactions and have also featured in dyes and catalytic reactions.^[2–4] For theoretical chemists paracyclophane has been a touchstone for years as it combines sp^2 and sp^3 hybridized carbon atoms in one molecule and also exhibits double and single bonds on an energetically very shallow hyperphase. Soon after it was first characterized by single crystal X-ray diffraction it also became obvious that the sp^3 hybridized carbon atoms in paracyclophane have very large Debye-Waller factors at temperatures above 90 K which lead to a discussion about a possible phase transition.^[5–6] Ever since, this phase transition and its origin have been in the center of very enthusiastic discussions between experimentalists and theoreticians.^[7–13] The two possible conformers of paracyclophane are depicted in Figure 1. Conformer **1** crystallizes in the centrosymmetric space group $P4_2/mnm$ and is stable at temperatures above 60 K. Conformer **2** crystallizes in the non-centrosymmetric space group $P\bar{4}n2$ and is the lowest energy structure as it freezes out below 45 K. The only difference between the two phases is the twist of the ethylene bridge. This twist has been first mentioned by Lonsdale *et al.*^[5] The first to describe a disordered model of the high temperature phase which modelled the two enantiomers of the low temperature phase were Hope *et al.*^[6]

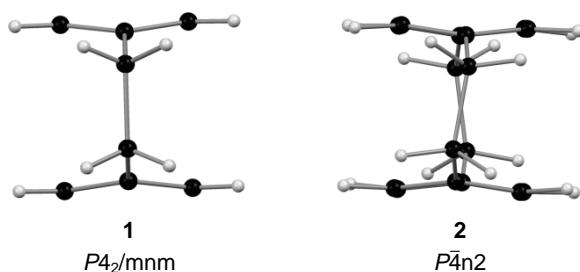


Figure 1. Centrosymmetric (left) and non-centrosymmetric phase (right)

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In a recent publication we were able to unambiguously establish the twisted structure to be the minimum structure as the crystal structure at 15 K shows a considerable twist of 12.7° (for definition of the angle see Supporting Information). Based on a heat capacity measurement indicating two phase transitions at 45 K and 60 K single crystal X-ray data were collected at various temperatures. These data clearly showed that the space group determination is not straightforward in the transition region between 45 and 60 K.^[14] Although analysis of these data suggests that a twisting motion of the ethylene bridges (see Supporting Information for definition) is the force that drives the phase transition this cannot be proven by means of X-ray

diffraction which gives an average over time and position over the whole crystal.

Spectroscopy is complementary to X-ray diffraction and is an excellent tool to study the vibrational parameters of a molecule^[15a] or a material.^[15b] Over the last 40 years there have been a number of spectroscopic studies on paracyclophane and its derivatives.^[16-19] However, none of them specially dealt with the characterization of the phase transition region although Westrum *et al.* reported a heat capacity measurement with an inflection around 50 K in 1970.^[20] Despite this, there have been reports dealing with a twist angle in the low temperature phase declaring the ground state or minimum structure to be of D₂ or D_{2h} symmetry.^[7,12-13,21]

In order to learn more about the phase transitions and the driving force behind the structural change we conducted simultaneous Raman spectroscopy and Inelastic Neutron Scattering (INS) at multiple temperatures at the TOSCA beamline at the ISIS Facility (STFC Rutherford Appleton Laboratory, UK). To the best of our knowledge there are no reported INS measurements of paracyclophane in the literature. To fully understand the nature of the phase transitions it is necessary to detect very subtle energetic changes. The symmetry of the low- and high-temperature conformers only differs in an additional mirror plane, hence their spectra are expected to be very similar. INS is the ideal tool for our study as it has no selection rules and thus detects all changes in the vibrational modes. Earlier spectroscopic studies (IR, Raman) on paracyclophane very often failed to measure spectra of high accuracy especially in the low energy region of a few hundred wavenumbers.^[13,16-17,21]

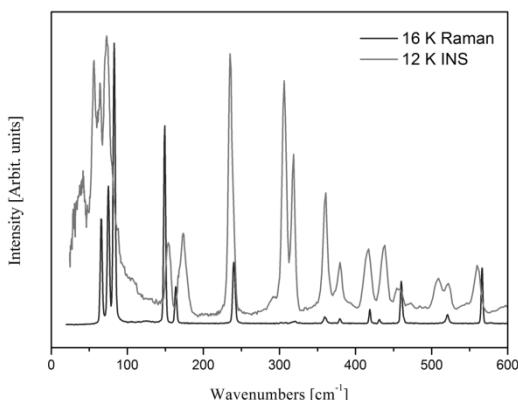


Figure 2: INS and Raman spectrum of paracyclophane at 12 K and 16 K respectively in the range of 0 to 600 cm⁻¹.

Due to the expected small differences between the spectra of the low- and high-temperature conformers it is this spectral region however, which is most likely affected by the phase transitions. This is also backed up by theoretical results which suggested the energetic difference between the two conformers to be as low as 0.2 kcal/mol.^[7,22-23] Simultaneous Raman and high resolution INS data were collected on a sample of finely ground powder at 12, 45, 55, 60 and 70 K. Additional Raman experiments were performed at 16, 30, 41, 45, 46, 50, 54, 59, 61, 71, 150, 152, and 300 K with a more powerful laser to give better resolution. A specially designed sample holder was cooled in a closed-cycle-

refrigerator installed in the spectrometer and a Raman laser was guided to the sample through an optical fibre.^[24] While the whole spectrum covers a range from roughly 20 to 3300 cm⁻¹ for the INS and from 40 to 3200 cm⁻¹ for the Raman spectra, the most important part is the low energy region as discussed above, this region is in the focus hereafter.

One can see at first glimpse that at 12 K a number of modes are Raman silent but INS active (Figure 2). Comparing these results with theoretical calculations it can be shown that the INS spectra are in excellent agreement with the calculated energies (Figure 3). Only a peak at 175 cm⁻¹ could not be assigned using the computational model based on the low-temperature crystal structure. In a publication of theoretically derived normal vibrations Walden and Glatzhofer assign the 175 cm⁻¹ peak to a 'ring rock around (the) y-axis "clamshell"'.^[7] It is also noteworthy that this peak disappears at temperatures above 54 K (see Figure 4).

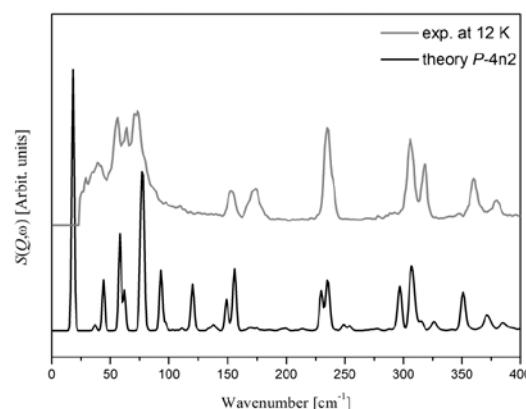


Figure 3: Experimental and theoretical INS spectrum of paracyclophane at 12 K in the range of 0 to 400 cm⁻¹.

Interestingly, this peak shows up in both the INS and the Raman spectra, which is a strong indicator that it is not an artefact. If the phase transition at 45 K is indeed driven by the twisting motion of the ethylene bridges, as has been proposed in our latest publication^[14], a clear difference should be visible in the INS and Raman spectra. Comparison of the 12 K INS spectra to one collected at 70 K (Figure 5), where the high symmetry phase is solely present, there are two significant differences. The broad peak at the very low energy region (60-100 cm⁻¹) of the INS spectrum weakens and loses its sharp features (Figure 5). With the well resolved Raman data the low energy region can be analysed further (See Figure 4). At the very low energy part of the spectrum it can be noticed that three well resolved peaks coincide at higher temperatures to form one broad and one sharp peak in the Raman spectra. The two peaks at 65 and 75 cm⁻¹ coincide above 58 K which indicates that these peaks might hold a reason for the discontinuity at 60 K in the heat capacity measurement. In a very recent publication Li *et al.* observed a similar behaviour only in the opposite direction when paracyclophane is subjected to high pressure at room temperature.^[25]

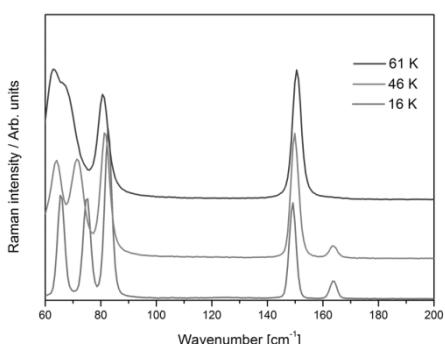


Figure 4: Temperature dependent Raman spectra for the low energy region (60 to 200 cm^{-1}).

The second substantial spectral change concerns a well-defined peak at roughly 750 cm^{-1} , which disappears when the temperature is increased slowly (See Supporting Information).

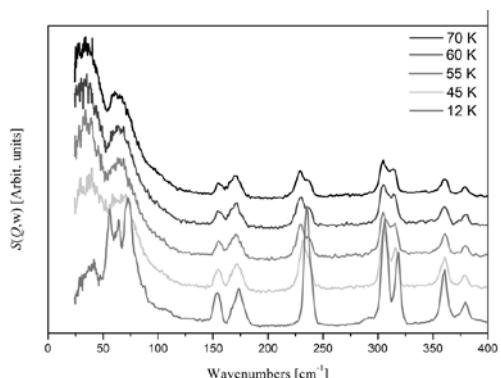


Figure 5: Temperature dependent INS spectra of paracyclophe in the range from 0 to 400 cm^{-1} .

These peaks at approx. 75 and 750 cm^{-1} match the calculated energies for twisting motions of the CH_2 -moieties of the ethylene bridges for the low temperature phase (calc.: 76, 78 and 749 cm^{-1}).

Another difference between the low- and high-temperature phases is observed at 240 cm^{-1} . It is surprising that this singlet mode splits up into a doublet at higher temperatures, *i.e.* at higher symmetry, according to Raman spectroscopy as well as INS (Figure 5 and 6 top). In fact, a doublet is present in the calculated spectrum (Figure 3) corresponding to a number of motions in this energy region. For the low-temperature phase two calculated energies (230 and 235 cm^{-1}) correspond to a twisting motion of the CH_2 -groups. Moreover, a pumping motion for the benzene rings towards and away from each other (see Supporting Information for definition) is proposed at similar energies (236 and 237 cm^{-1}). In the high-symmetry phase there is only one calculated peak for the CH_2 -group twist (224 cm^{-1}) and two for the pumping motion (237 and 238 cm^{-1}). Although the splitting feature is more prominent in the Raman spectra, it is also clearly observed in the INS spectra. In their high pressure study Liu *et al.* observe no peak at 240 cm^{-1} below pressures of 3.9 GPa but the appearing peak splits above pressures of 3.9 GPa . They

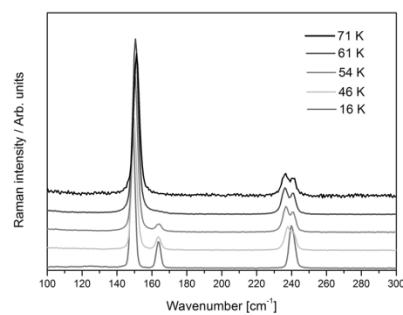


Figure 6: Temperature dependent Raman spectra of paracyclophe in the range of 100 to 300 cm^{-1} (top) and 1100 to 1300 cm^{-1} (bottom).

speculate about a phase transition towards the low symmetry phase with D_2 symmetry induced by high pressure above 3.9 GPa which would explain their spectra. Although this is in contrast to our observations all other reported peaks are in excellent agreement with our study, using pressure instead of temperature as a probe.

A more puzzling difference is a small sharp peak at around 1220 cm^{-1} , which also disappears above 40 K (Figure 6). Again, this peak has no exact counterpart in the calculated energies. For the low-temperature phase Raman active modes were calculated at 1202 - 1207 cm^{-1} and at 1242 - 1255 cm^{-1} . Furthermore, Li *et al.* also report this peak for pressures above 3.9 GPa . Unfortunately, much like us they are not able to explain the physical origin of this peak. Walden and Glatzhofer assign this peak to a stretching motion of the bridging carbon to the ring carbon and a bending of the aromatic hydrogen atoms. Unfortunately, the INS spectra are noisy in this energy region so we cannot confirm the presence of this peak in the INS data.

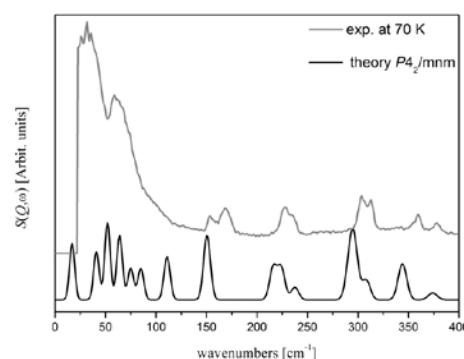


Figure 7: Experimental and theoretical INS spectra for the high symmetry phase in the range of 0 to 400 cm^{-1} .

It is noteworthy that the high temperature phase calculations resulted in four imaginary modes at low wavenumbers which correspond to the twisting of the ethylene bridge and the pumping of the molecule. The resulting imaginary modes are due to the fact that these are 0 K calculations and that the high-temperature phase is not stable at this temperature. However, this is also a very strong sign that it is indeed this twisting motion which is responsible for the phase change. The calculated wavenumbers for the higher energy modes are not affected by this and can correctly be assigned.

Another conclusion that we were not able to answer from crystallography unambiguously is whether the symmetry change is induced by a dynamic or static disorder of the ethylene bridge. From the spectroscopic data in hand now it is clear that we do indeed observe a twisting motion of the bridges in both the low and the high symmetry phase. The motion is so fast that it results in a crystal structure with the higher symmetry and a large displacement parameter for the bridging carbon atom at high temperature.

Unfortunately, we were not able to gain more insight into the second phase transition at 60 K. Although there are small changes observable in the spectra between 54 and 60 K the peaks affected cannot be assigned to a certain motion that would explain a second phase transition.

Experimental Section

INS and Raman Experiment

Experiments were conducted at the TOSCA beamline in Target Station One at ISIS Rutherford Appleton Laboratory, Didcot, UK. TOSCA is an indirect geometry spectrometer equipped with 130 squashed ^3He tubes as detectors and the beam has an energy range from -20 to 8000 cm^{-1} .

2.1 g of finely ground single crystals of [2,2]-paracyclophane were packed into aluminium foil and put into the aluminium sample holder. The custom made center stick was lowered into the neutron beam and the spectrum recorded for approximately 4 h at each temperature. The temperature is controlled via a closed cycle refrigerator. Simultaneous^[10] Raman and inelastic neutron scattering data were collected at 12, 45, 55, 60 and 70 K. Additional Raman spectra were collected offline to cover the temperature range up to room temperature. The Raman spectra were recorded with a Renishaw inVia spectrometer incorporating a 300 mW Toptica 785 nm wavelength stabilized diode laser. The Raman spectra were collected with 100 % laser power and confocal mode collecting signals every 30 seconds for the duration of the INS measurement. After data collection the Raman spectra were corrected using a Raman response curve in order to account for different sensitivities at different wavenumbers. The offline Raman measurements were made with the same Raman system that had been upgraded to allow measurements as low as 40 cm^{-1} Raman shift and with improved resolution over the 40 – 1800 cm^{-1} range. Therefore, only these Raman data are used throughout the paper. The Raman spectra did not show differences apart from the better resolution in the low energy region.

Computational Methods

Periodic density functional theory (periodic-DFT) calculations were carried out using a plane wave basis-set and pseudopotentials as implemented in the CASTEP code.^[12] The refined crystal structures at 15 ($P\bar{4}n2$) and 120 K ($P4_2mn$) were used as the initial input structures. The generalised gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) functional was used in conjunction with optimised norm-conserving pseudopotentials with a plane-wave cut-off energy of 750 eV, the k-point sampling used a $4\times4\times4$. Monkhorst-Pack grid and the forces were converged to better than $|0.005| \text{ eV } \text{\AA}^{-1}$. Phonon modes were calculated using density-functional perturbation-theory.^[13] As a prerequisite to any lattice dynamics calculation a full geometry optimization of

the internal atomic co-ordinates was performed. The output of the phonon calculation includes infrared intensities and the atomic displacements of the atoms in the mode. The visualisations of the Cartesian nature of these modes were carried out in Materials Studio (Accelrys)^[14] or using Jmol^[15] and the INS spectra were generated with ACLIMAX.^[16]

Acknowledgements

H. W. and D. S. are grateful to the DNRF funded Center for Materials Crystallography for financial support. N. L. would like to thank the Villum Foundation for financial support. Experiments at the ISIS Pulsed Neutron and Muon Source were supported by a beamtime allocation from the Science and Technology Facilities Council. This research project has been supported by the European Commission under the 7th Framework Programme through the 'Research Infrastructures' action of the 'Capacities' Programme, NMI3-II Grant number 283883. Contract No. 283883-NMI3-II.

Keywords: non-destructive phase transition • paracyclophane • inelastic neutron scattering • Raman spectroscopy • structure determination

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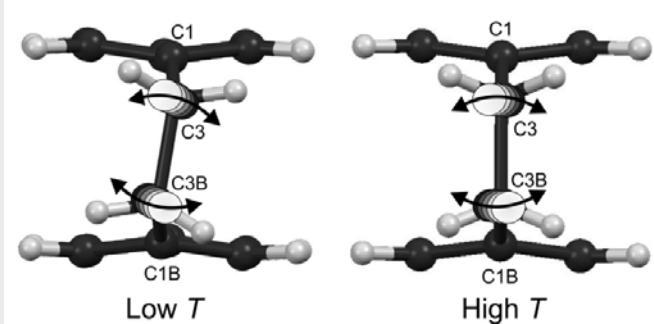
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Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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COMMUNICATION



The **high temperature phase** calculations ($T > 60$ K) of [2,2]-paracyclophane result in four imaginary modes at low wavenumbers which correspond to the ethylene bridge twisting and the pumping of the molecule. However, this is a strong sign that it is this twisting motion which is responsible for the phase change, because the high temperature phase is not stable at 0 K. This was shown by combined Raman and Inelastic Neutron Scattering experiments from 12 to 300 K.

Cyclophane Phase Transition

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Direct Spectroscopic Evidence of the Mechanism behind the Phase Transition of [2,2]-Paracyclophane

Supporting Information

Direct Spectroscopic Evidence of the Mechanism behind the Phase Transition of [2,2]-Paracyclophane

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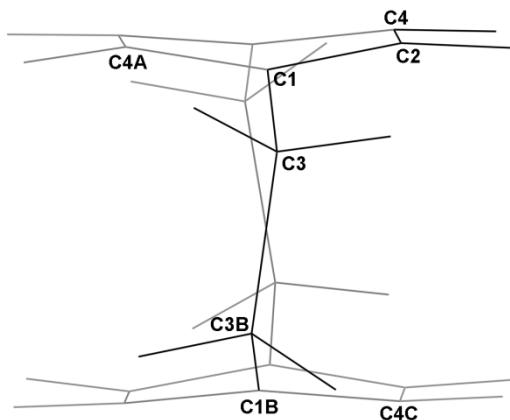


Figure 1: Sketch of paracyclophane for twist angle definition. Twist angle definition: C1–C3–C3B–C1B

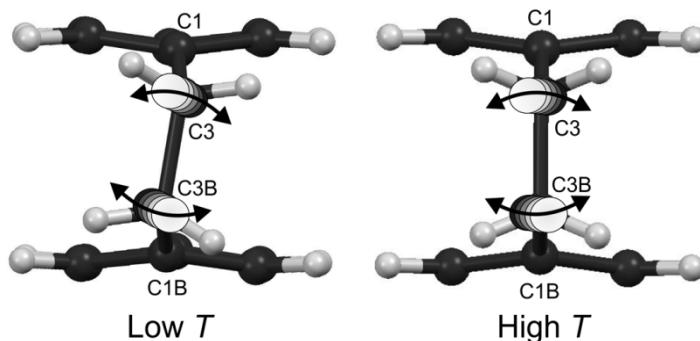


Figure 2: Twisting motion as described by the ethylene bridges.

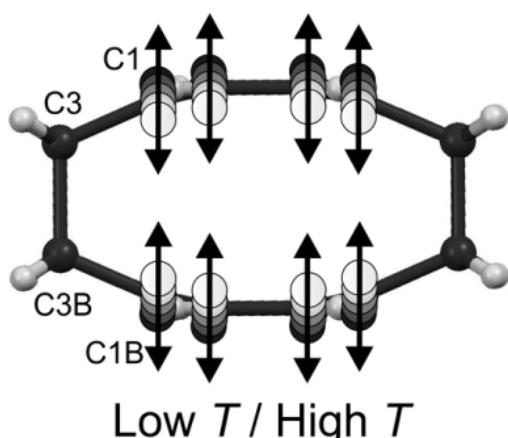


Figure 3: Pumping motion as described by the benzene rings.

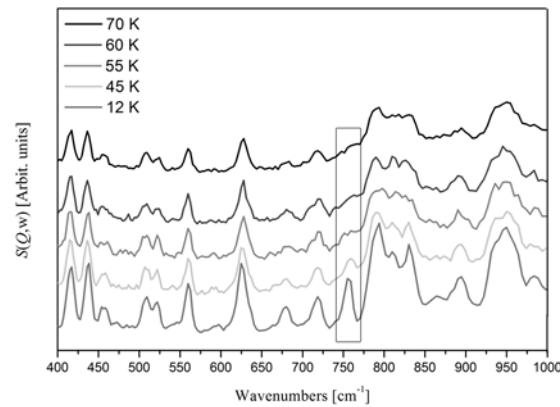


Figure 4: Temperature dependent INS spectra of paracyclophane from 400 to 1000 cm^{-1} .

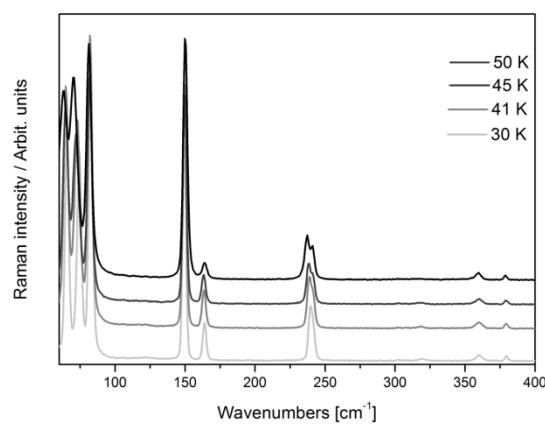


Figure 5: Temperature dependent Raman spectra of paracyclophane from 60 to 400 cm^{-1} .

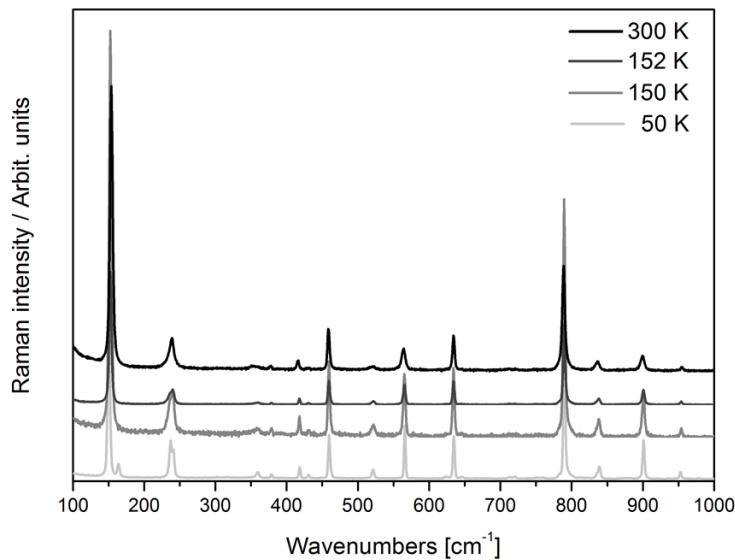


Figure 6: Temperature dependent Raman spectra of paracyclophane from 100 to 1000 cm^{-1} .

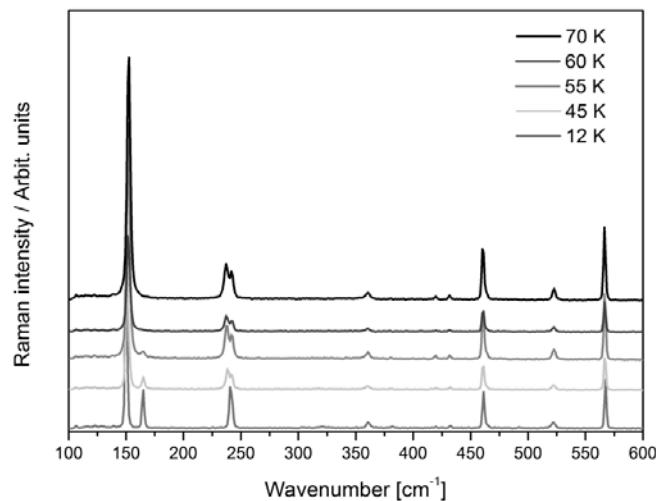


Figure 7: Temperature dependent Raman spectra in the range of 100 to 600 cm^{-1} as detected with the less powerful laser simultaneously with the INS spectra.