



	Experiment title: Pressure-induced Diels-Alder reactions probed by XRD	Experiment number: CH1226
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Report:

In **CH-1226** we studied the x-ray diffraction behaviour of pressure-induced Diels Alder reactions. The system of investigation was naphthalene / tetracyanoquinodimethane (naph-tnq). In some respect this reaction is complementary to [2+2] photodimerisation reactions as the reaction can be triggered by temperature or pressure [1-4]. However, structural related questions concerning the mechanism of the reaction, like the size of the activation volume for the reaction provided by the crystal lattice and the remaining of the periodic structure over the entire lattice and during the transformation process are the same or of similar kind.

Till now most of the studies performed were done in the optical, namely infrared regime [5,6]. By probing the decrease of the phenyl doublebond-stretch on naphthalene and/or the increase of an additional C-C single bond stretching vibration it was possible to follow the decrease of the reactant and increase of product concentration as a function of pressure / temperature. Aim of this study was to monitor the whole – or at least most accessible - structural response function during the pressure-induced Diels Alder reaction.

The pressure-dependent powder diffraction data showed significant changes by going from 10 kbar to 15 kbar. This is the pressure regime to be known to decrease the distance between naph and tcnq in such a way,

that Diels-Alder reactions become possible. However, above 15 kbar no dominant changes in the diffraction pattern were observed anymore. We realised quite late, that the single crystal structure of naph-tcnq was unknown and had to be solved, first. After doing this “home-work” we could refine the powder diffraction data which essentially monitors the unit cell changes upon pressure change, and the relative distance changes between naphthalene and tcnq. At pressure values of 13.5 kbar, which were monitored by the ruby method, the distance between naphthalene and tcnq decreased from about 4.2 Å to 3.8 Å making the Diels-Alder reaction possible. Over a quite narrow pressure range of about 5 kbar the whole crystal transformed from the pure naphthalene and tcnq single reactant molecules to the product adduct. During the pressure-induced transformation no diffuse planes were observed.

We hope to submit these results in near future [7,8].

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