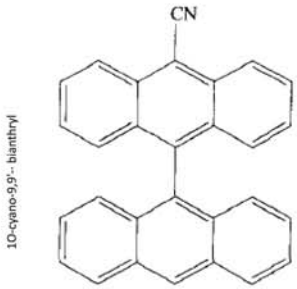
Structure of Organic (CNBA) molecules

The CNBA pre-twisted conformation is responsible for its excited state dynamics



The photo-optical properties of 9,9'-bianthracene-10-carbonitrile (CNBA) in solution are related to the angle between the two anthracene moieties. The 9,9'-bianthryl and its analogues are well-known systems whose excited state behavior and dynamical processes have been studied extensively in a range of conventional solvents. The interest in 9,9'-bianthryl and its analogues is mainly due to the fact that this pre-twisted molecule with mutually perpendicular anthracene rings in the ground state undergoes symmetry breaking upon excitation and its fluorescence spectra shows distinct charge transfer character, especially in polar solvents. In nonpolar solvents the first excited state is predominantly a locally excited state with very little or no character, whereas, in highly polar solvents a charge transfer state, which is formed rapidly from the locally excited state, is the emitting state.

The challenge:	small nanocrystals; light atoms in the structure; beam sensitivity
Solution:	Automated 3D diffraction Tomography with beam precession using a cryo-holder

Information about the conformation of CNBA in the solid state can normally be obtained by X-ray crystallography. However, for many of these materials transmission electron microscopy (TEM) and electron diffraction are the only techniques because they can deliver structural information from areas as small as tens of nanometers.

While high resolution transmission electron microscopy (HRTEM) normally cannot be used with organic materials due to their fast deterioration under strong beam conditions, electron diffraction requires only a fraction of such electron dose rate on the sample. Thus, Automated 3D Electron Diffraction tomography data collection was used for structure determination of CNBA. Electron crystallography of organic materials is especially powerful, for instance, when working with polymorphic systems.

The 3D diffraction tomography data were collected in a tilt range of 120 degrees (±60 degrees), delivering a coverage of two thirds of the complete reciprocal volume. A resolution of 0.8 Å was recorded with 9415 reflections being measured which reduced to 3519 independent reflections after merging symmetry equivalents, with an Rmerge of 21.77%. Tomography data confirmed the cell parameters and allowed recognition of the space group P21 /c and solution of the structure. All the atoms (carbon and nitrogen) were detected a*b initio* with a final R of 24%.

The molecule has a rather rigid conformation. The only degree of conformational freedom is the torsion angle between the two anthracene moieties. The anthracene fragments were found basically in a flat geometry, but additional refinement of the geometry was necessary. Structure refinement was performed in SHELXS. The refinement delivered a torsion angle between the anthracene moieties of 93.8 degrees. Electron diffraction is a well-known and extremely powerful method to gain structural information from beam-sensitive materials. Although the instability of the material under irradiation means that extra care has to be taken, electron diffraction data can be collected by optimizing the acquisition conditions and result in *ab initio* structure determination

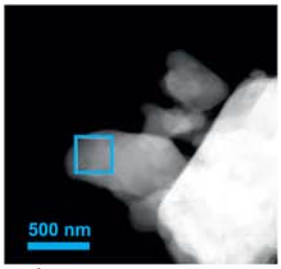
Crystal Structure

$C_{29}H_{17}N$

Monoclinic $P2_1/c$
a= 14.7 Å
b= 9.5 Å
c= 15.4 Å
β= 112.0°

Experimental data

tilt range: ±60° step: 1°
No indiv. reflections: 3519
No indiv. atoms: 30
R = 24%



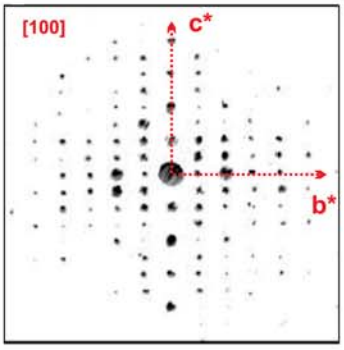


figure 1

Crystal Area Where Data collected & 3D Reconstructed Data of CNBA

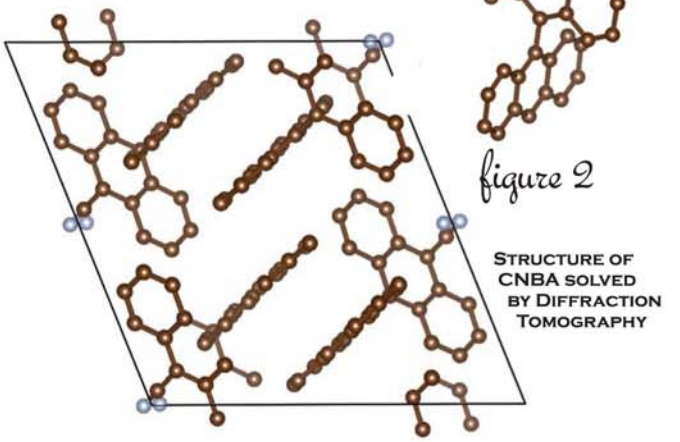


figure 2

Structure of CNBA solved by Diffraction Tomography

U. Kolb et al *Polymer Reviews* (2010) 50 385-409