X-Ray Structure Determination

A colorless thin plate (0.35 x 0.26 x 0.04 mm^3) was used for the single crystal x-ray diffraction study of mm7r ($C_{24}H_6Cl_6S_6$.C4H8O, KYI-CHT). The crystal was mounted on to a glass fiber with epoxy resin. X-ray intensity data were collected at 213(2)K on a Bruker SMART 1000 (**ref. 1**) platform-CCD x-ray diffractometer system (Mo-radiation, λ = 0.71073 Å, 50KV/45mA power). The CCD detector was placed at a distance of 3.9730 cm from the crystal.

A total of 1321 frames were collected for a hemisphere of reflections (with scan width of 0.3^o in ω and ϕ angles of 0^o, 90^o, 180^o, and 0^o for every 606, 435, 230, and 50 frames, respectively, 60sec/frame exposure time). The frames were integrated using the Bruker SAINTPLUS software package (**ref. 2**) and using a narrow-frame integration algorithm. Based on an orthorhombic crystal system, the integrated frames yielded a total of 12941 reflections at a maximum 2θ angle of 56.56^o (0.75 Å resolution), of which 4067 were independent reflections (R_{int} = 0.0660, R_{sig} = 0.0579, redundancy = 3.2, completeness = 99.7%) and 2639 (64.9%) reflections were greater than 2σ(I). The unit cell parameters were, **a** = 24.646(5) Å, **b** = 10.612(2) Å, **c** = 13.602(3) Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 3557.6(12) $Å^3$, Z = 8, calculated density D_c = 1.575 g/cm^3. Absorption corrections were applied (absorption coefficient, μ = 0.867 mm^{-1}; max/min transmission 0.9662/0.7513) to the raw intensity data using SADABS (**ref. 2**).

The Bruker SHELXTL (Version 5.1) software package (**ref. 3**) was used for phase determination and structure refinement. The distribution of intensities (E^2-1 = 0.879) and systematic absent reflections indicated two possible space groups; Cmca and Aba2. The space group Aba2 was later used for the final structure refinement. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. The structure was refined with both space groups; Cmca (R1=0.0826) and Aba2 (R1=0.0749).

For the centro-symmetry space group Cmca, only one quarter of the molecule was in the asymmetry unit of the unit cell. One Cl and one C atom were located on the mirror plane. From the difference electron density map and using mirror plane symmetry operator, half a molecule of an enantiomer was generated and the bond lengths and angles were refined with restraints. The other enantiomer was the mirror plane symmetry image. The site occupancy factors (SOF) for all the atoms were fixed at 50%. During refinement, the mirror plane symmetry constraint was suppressed for the molecule so that those atoms bonded to mirror plane symmetry generated atoms were excluded. The refinement converged to R1=0.0845.

For the non-centrosymmetry space group, Aba2, one half of the molecule was in the asymmetry unit of the unit cell. Both enantiomers were identified from the electron density map. The SOF for all the atoms of each enantiomer was fixed at 50%. The bond lengths and angles were refined with restraints. This space group model gave a better fit to the experimental data and the refinement converged to R1=0.0749 (for space group Cmca, R1=0.0845). The space group, Aba2 was the most probable space group where the molecule was not located on a mirror plane.

A disordered solvent of tetrahydrofuran was found and the SOF of all the atoms was fixed at 50%. The bond lengths and angles were refined with restraints. Because the molecule did not have a local mirror symmetry and the all bond lengths and angles were refined with restraints

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. All the H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at R1 = 0.0749, wR2 = 0.2001, with intensity, $I>2\sigma(I)$. The largest peak/hole in the final difference map were 0.787/-0.342 $Å^3$.

REFERENCES

1. SMART Software Reference Manual, Version 5.054, Bruker Analytical X-Ray System, Inc., Madison, WI 1997-1998.

2. SAINTPLUS Software Reference Manual, Version 5.02, Bruker Analytical X-Ray System, Inc., Madison, WI 1997-1998.

3. SHELXTL Software Reference Manual, Version 5.1, Bruker Analytical X-Ray System, Inc., Madison, WI 1997-1998.