### Experimental

#### Data collection and refinements

A single crystal of 1, 0.20 × 0.15 × 0.11 mm, was selected for measurement. Diffraction data were collected on an automated CCD diffractometer, Rigaku AFC-8 Mercury, on PF-AR NW2 beam line at KEK using 0.7000 Å radiation with an oscillation method at 106K. Bragg spots on the imaging plates were integrated up to $\sin \theta / \lambda = 0.97$ Å$^{-1}$, and scaled with the program HKL2000. Measured and independent reflections, $R_{int}$ and completeness were 124265, 22754, 0.0401 and 0.915, respectively.

The reported structure was used as an initial model. Anomalous scattering factors and X-ray absorption coefficients were taken from references 3 and 4, respectively. Following the refinements, high order refinements were carried out using all 9818 independent reflections with $\sin \theta \lambda \geq 0.60$ Å$^{-1}$ with the program SHELXL97. Positions of hydrogen atoms were constrained to have C–H distances of 1.092, 1.083 and 1.059 Å for methylene, aromatic and methyl groups, respectively. Refinements of multipole expansion method using the Hansen-Coppens multipole formalism and topological analyses based on resulted parameters were performed with the XD package. Refinement was carried out against 6915 independent reflections of $\sin \theta / \lambda \leq 0.8$ Å$^{-1}$ with $I > 3\sigma(I)$ based on $F^2$. At the first stage of the refinements, atomic coordinates and $U_{ij}$ of non-hydrogen atoms were fixed on those of the high order refinement, and $U_{iso}$ of hydrogen atoms were fixed on 1.2$U_{eq}$ and 1.5$U_{eq}$ of each parent C atom for methylene and aromatic, and methyl groups, respectively. At the first stage of the refinements, the population parameters, $P_v$, $P_{lms}$ of non-hydrogen atoms and scale were refined. Levels of multipoles were raised stepwise up to hexadecapole and octupole for Zr and C atoms, respectively. On the refinements of the population parameters were constrained by assuming the molecular $C_2$ symmetry. At the second stage, radial screening parameters, $\kappa$ and $\kappa'$ for non-hydrogen and hydrogen atoms were refined. At the third stage, the levels of multipoles were raised stepwise up to hexadecapole, octupole and dipole along the bond for Zr, C and H atoms, respectively. After those refinements, the second and third strategies were repeated twice and finally the $P_v$, $P_{lms}$, $\kappa$, $\kappa'$, coordinates of the non-hydrogen atoms and temperature factors and scale were refined. The positions of the H atoms were constrained to have C–H distances of 1.092, 1.083 and 1.059 Å for methylene, aromatic and methyl groups, respectively. The number of parameters in the final cycle of the refinements was 425. A molecule electro-neutrality constraint was applied all through the refinements.

### References