Electronic Supplementary Information

Investigation on the vibrational and structural properties of a self-structured bridged silsesquioxane

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Details of the crystal structure determination
The data was characterized by a relatively steep drop in intensity with increasing diffraction angle. The space group R-3 was assigned based on E statistics (mean |E^2-1| = 0.957 to 0.84 Å resolution) and systematic absences. An initial structural model was obtained using the charge flip procedure in P1. Inspection of the electron density so obtained indicated the presence of threefold inversion axis symmetry in the unit cell and revealed the positions of the C, N and O atoms of the ureidopyrimidinone backbone. Difference Fourier syntheses, which were carried out in R-3 after least squares refinement of the partial structure indicated extensive disorder of the side chain bearing the tris(ethoxysilyl) group. Maximum entropy electron density synthesis, using the observed structure factor amplitudes, combined with phases from the model without the side chain, and a flat prior, gave distinct atomic maxima for the ureidopyrimidinone backbones. Rather diffuse electron density was apparent around the 3 axis (see figure 1c), which is obviously due to the disordered C_2H_4Si(OEt_3) side chains. Several maxima in this region can be assigned to partially occupied positions of the silicon atoms (which were not included in the model used to generate the phases). In addition, solvent of crystallization could be present. Attempts to model this disorder with various split-atom schemes did not give satisfactory results. For further calculations, hydrogen atoms were added to the ureidopyrimidinone moiety in calculated positions (refined riding). Refinement with anisotropic displacement parameters for the non-hydrogen atoms converged to R(F) = 0.4 when the C_2H_4Si(OEt_3) side chain was omitted from the model. Addition of this substituent to the model, with an internal geometry highly restrained to sensible values and with isotropic atomic displacement parameters, reduced R(F) to 0.26. To try to obtain more reliable geometric parameters for the ureidopyrimidinone dimers, the electron density due to the disordered chain was treated with the BYPASS procedure, and so effectively removed from the data. Refinement of the non-disordered part of the structure against the modified F_{obs} converged to R(F) = 0.090, wR(F^2) = 0.2764, GooF = 0.953.

References

1. We are aware that molecular crystals with apparent trigonal symmetry are often twinned (see for example: R. Herbst-Irmer, G. M. Sheldrick, Acta Cryst., 1998, B54, 443). However, in the present case the typical warning signs for twinning - a very low value of |E^2-1| and an only slightly higher merging R_{int} value for the higher symmetric Laue group(s) (-3m1, -31m) - were absent.


5. L. Palatinus and S. van Smaalen, BayMEM, University of Bayreuth, 2005.


12. We note that this procedure is not completely satisfactory, because of the large number of electrons involved and its deficiencies in treating the region where the “squeezed” side chain connects to the ordered part.