Comparison of a Conventional and Synchrotron X-ray Structure Determination of [1,2,4,5-tetrahydroxybenzene] [2,5-dihydroxy-1,4-benzoquinone]

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Introduction

Because of our interests in the synthesis of elaborated porphyrins as models for the heme active sites in myoglobin, we synthesized the precursor [1,2,4,5-tetrahydroxybenzene] [2,5-dihydroxy-1,4-benzoquinone] (I). Crystals of (I) are stable and of excellent quality. Consequently, a short wavelength (0.354 Å) data set was collected from a crystal of (I) on the Rigaku R-axis image plate diffractometer at the Advanced Photon Source (APS). Refinement of this data set provides a check on the APS system and an interesting comparison with the results from a conventional structure determination.

Methods and Materials

Crystals of compound (I) were prepared by a allowing a small quantity of [1,2,4,5-tetrahydroxybenzene][H_2O][1] to stand in D_2O for 1 month. Conventional x-ray data for compound (I) were collected at 163K on an Enraf-Nonius CAD-4 diffractometer by standard methods on a crystal of dimensions 0.43 x 0.15 x 0.05 mm. Synchrotron data for compound (I) were collected at 110K on an R-axis IV image plate detector at the 5-BM-B beamline hutch of the DND-CAT at the APS on a crystal of dimensions 1.12 x 0.33 x 0.20 mm. The crystal-to-detector distance was 165.0(1) mm, and the beam size was 2 mm by 2 mm. Each frame covered 6° in ϕ for 2 minutes. Data were collected in one group of 20 frames starting at a ϕ setting of 0°. Raw data were corrected for angular variation of the phosphor response of the image plate with a local program, following the method of Zaleski et al.[2] For both data sets, anisotropic displacement parameters were used for non-hydrogen atoms. H atoms were refined isotropically.

Results

In compound (I), molecules of [1,2,4,5-tetrahydroxybenzene] and [2,5-dihydroxy-1,4-benzoquinone] are both located on inversion centers in space group $P2_1$ /n. Hence the benzene and quinone portions of these molecules are planar by symmetry. They are tilted relative to each other by 64.00(5)° as measured by their mean planes. The two kinds of molecules (Fig. 1) alternate to form two unique stacks parallel to the a-axis and two unique stacks parallel to the b-axis

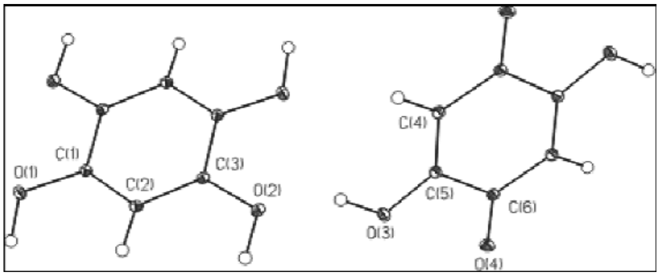

FIG. 1. The numbering scheme for [1,2,4,5-tetrahydroxybenzene] [2,5-dihydroxy-1,4-benzoquinone].

For compound (I), the results from the conventional x-ray determination are in very good agreement with those from the synchrotron x-ray determination (Table I). There are a few possibly significant differences, e.g., C2-C3 (1.389(2) Å vs.1.3953(4) Å), but, since the conventional data were collected at 163K and the synchrotron data at 11 K, it is possible that these arise from differences in vibrational foreshortening of the bonds. In this regard, if a linear correction is applied for the differences in temperature[3] then generally the anisotropic displacement paramters U_{ij} from the two determinations agree within about 10%. Since in x-ray structure determinations it is the U_{ij} that are most sensitive to a variety of systematic errors, we find this agreement very encouraging. The estimated standard deviations associated with quantities derived from the synchrotron data (5678 independent reflections) are roughly 20% of those derived from the conventional data (842 independent reflections).

Table I. Comparison of selected geometrical parameters.

Distance (Å)	Conventional Data	Synchrotron Data
O1–C1	1.367(2)	1.3635(3)
O2-C3	1.374(2)	1.3710(3)
O3-C5	1.332(2)	1.3289(3)
O4-C6	1.236(2)	1.2386(3)
C1-C2	1.386(2)	1.3923(4)
C1-C3'	1.394(2)	1.3994(4)
C2-C3	1.389(2)	1.3953(4)
C3-C1'	1.394(2)	1.3994(4)
C4-C5	1.341(2)	1.3533(4)
C4-C6''	1.440(2)	1.4423(4)
C5-C6	1.505(2)	1.5011(4)

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References

[1] W.K. Anslow and H. Raistrick, J. Chem. Soc. 1446-1457 (1939).

[2] J. Zaleski, G. Wu, and P. Coppens, J. Appl. Cryst. **31**, 302-304 (1998).

[3] J.D. Dunitz, V. Schomaker, and K.N. Trueblood, J. Phys. Chem. **92**, 856-867 (1988).