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A Packing Relationship Between 1,4-Dibenzyloxybenzene and 4-Benzyloxyphenol

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Molecular compounds of a given homologous series often assume closely related modes of packing in the solid state. Kitaigorodskii[1] has called this phenomenon "homologous isomorphism", and it is readily detectable from unit cell parameters. The molecules must be aligned with, or tilted only slightly from, one of the cell directions. Then two cell dimensions of the members of the homologous series are nearly equivalent in size, while the third reflects a change in the length of the molecule; the space groups of the members of the series are often identical. An example of such a series of compounds is biphenyl, terphenyl and quarterphenyl.[2] All crystallize in space group $P2_1/c$ with both the b and c dimensions within ± 0.1 Å of each other; and a, the long axis, measured as 9.39 Å, 13.7 Å and 17.8 Å, respectively.

It can be deduced from cell parameters of 1,4-dibenzyloxybenzene and 4-benzyloxyphenol, that the packing similarities described above can exist between molecular compounds which are not members of the same homologous series. The cell dimensions and space group of 1,4-dibenzyloxybenzene and 4-benxyloxyphenol were determined from X-ray diffraction precession photographs. The crystals were fragile, thin plates grown from ethanol solution. Cell parameters for 1,4-dibenzyloxybenzene are $a = 17.6 \pm 0.1$ Å, $b = 5.70 \pm 0.05$ Å, $c = 7.84 \pm 0.05$ Å, $\beta = 95.5 \pm 1.5°$; for 4-benzyloxyphenol, cell parameters are $a = 23.42 \pm 0.05$ Å, $b = 5.50 \pm 0.05$ Å, $c = 7.94 \pm 0.10$ Å, $\beta = 90.5 \pm 1.0°$. In both crystals the space groups, $P2_1/c$, is established by systematic absences and the plane of the mirror is perpendicular to the plate of the crystal. The number of

molecules per unit cell, Z, is 2 in 1,4-dibenzyloxybenzene, but 4 in 4-benzyloxyphenol.

With $Z = 2$, the center of a 1,4-dibenzyloxybenzene molecule is located at $\bar{1}$ positions, e.g., set a for the space group as listed in the International Tables;[3] the ends of the molecule are then related through the centers of symmetry, set b. Molecular models reveal that 1,4-dibenzyloxybenzene can easily assume a planar or near planar conformation. Moreover, the length of 1,4-dibenzyloxybenzene, including terminal van der Waal distances, is roughly 17.5 Å; and, therefore, the molecule must be approximately aligned with the a axis. The other cell dimensions are also consistent with this alignment. Biphenyl has a similar molecular cross-section, and its cell constants are $b = 5.51$ Å and $c = 8.04$ Å.

The cell dimensions of 4-benzyloxyphenol are those that would be expected for the next member in homologous sequence with 1,4-dibenzyloxybenzene, namely,

$$C_6H_5—CH_2—O—C_6H_4—O—CH_2—C_6H_4—O—CH_2—C_6H_5.$$

This latter molecule has an overall length of about 23.5 Å. The a-axis length observed for 4-benzyloxyphenol can be accounted for as follows. Dimers, which are extended along the a axis, pack in the solid. These associate through their phenol groups and are symmetrically located around $\bar{1}$ positions. The space filling shape of the phenol groups then serves to substitute for the volume occupied by the $-O—CH_2-$ linkage between the middle phenyl rings in the higher homologue. With such a group substitution, an apparent homologous isomorphism exists between 1,4-dibenzyloxybenzene and 4-benzyloxyphenol.

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