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THE CRYSTAL STRUCTURE OF 3-HYDROXY-4-METHOXYBENZALDEHYDE (ISOVANILLIN)

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The crystal structure of isovanillin was determined by a three-dimensional X-ray analysis. The molecules are linked by the O-H···O hydrogen bond (2.741 Å) between the hydroxyl and aldehydic groups and form a linear chain approximately perpendicular to the b axis and parallel to the (201) plane.

As a part of the program of studies on the structures of vanillin and its isomers, the crystal structure analysis of 3-hydroxy-4-methoxybenzaldehyde (isovanillin) was undertaken in order to determine the molecular conformation and the hydrogen bonding scheme.

The crystals were grown from an aqueous solution of commercially available isovanillin. The crystal data are: $C_8H_8O_3$, M.W.=152.15; monoclinic, a=8.517 (3), b=13.380 (5), c=6.390 (3) Å, β=97.21 (5)°, V=722.4 Å^3; Z=4, D_x=1.399, D_m=1.40 g.cm^{-3}; space group $P2_1/a$. The intensity data were collected on a RIGAKU automatic four-circle diffractometer with MoKα radiation monochromatized by means of a graphite monochrometor. The reflections within the range of $2\theta \leq 55^\circ$ were measured by the ω-2θ scan technique. A total of 1354 reflections was obtained, which had intensities greater than three times their standard deviations.

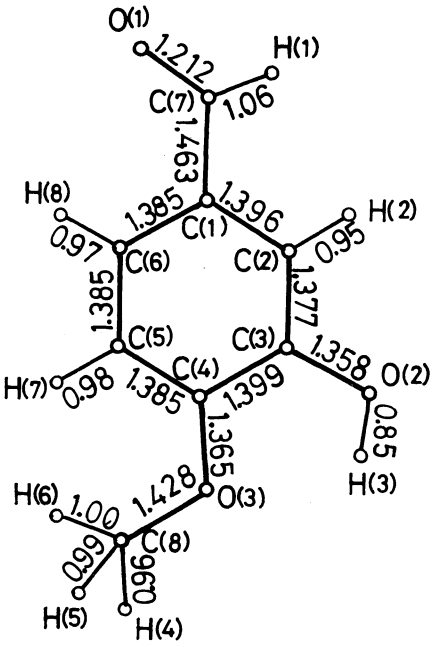
The structure was solved by a symbolic addition method[1] using the program DP-system written by R. S. Hall. All hydrogen atoms, including those of the methyl group, were found from a difference Fourier map. Block-diagonal least-squares refinement with anisotropic temperature factors for carbon and oxygen atoms and with isotropic temperature factors for hydrogen atoms were carried out and the R value was reduced to 0.040 for all observed reflections.

Bond lengths and angles are shown in Fig. 1. Standard deviations in the bond distances and angles between heavy atoms are 0.002 Å and 0.15°, respectively. Standard deviations in those relating to hydrogen atoms are about 0.02 Å in the bond distances and about 1° in the bond angles. The average C-C bond distance in the benzene ring (1.388 Å) is close to the value found in benzene, 1.392 Å[2], but the C(2)-C(3) distance (1.377 Å) is shorter than the rest of the benzene ring distances (average value: 1.390 Å). The benzene ring (I) is planar, deviations being within 0.01 Å. The aldehydic group (II) and the methoxy group (III) are almost coplanar with the benzene ring, while the plane of hydroxyl group (IV) including hydrogen atom is not. The dihedral angles between planes: I and II, I and III, and I and IV, are 2.5, 1.0 and 13.3°, respectively.

Fig. 2 shows the molecular arrangement viewed along the c axis. The molecules are linked by the O-H···O=C hydrogen bond and form a linear chain approximately perpendicular to the b axis and parallel to the (201) plane. The distance of the hydrogen bond, O···O, is 2.741 Å and the angle of O-H···O is 150°.

At the final stage of refinement, a three-dimensional difference synthesis including all the atoms was calculated. The resulting map revealed the residual electron density maxima corresponding to the bonding electrons.

A detailed discussion on this structure as well as the bonding electrons will appear elsewhere.



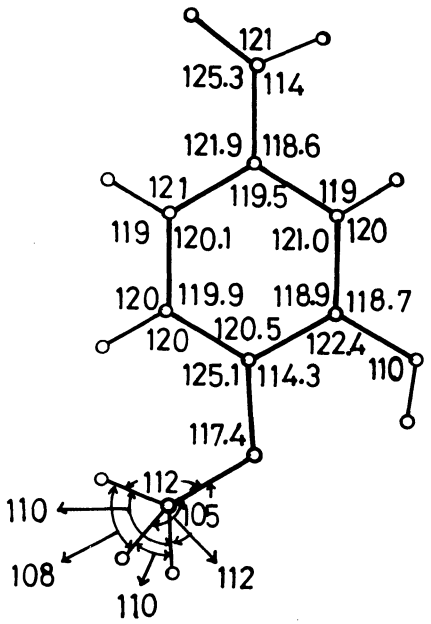


Fig. 1 Bond distances and angles.

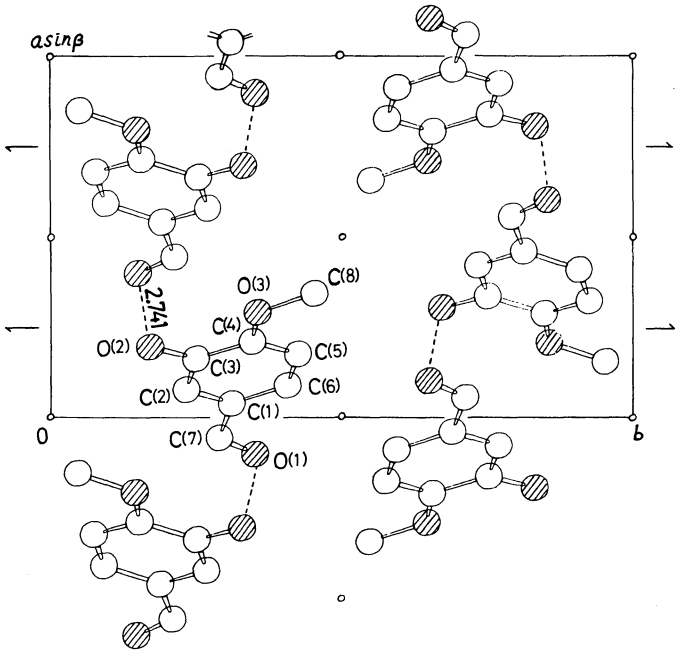


Fig. 2 The crystal structure viewed along the c axis.

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References

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