The Crystal Structures of Pentaglycerol and Neopentylglycol

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(Received August 9, 1969)

We have made a structural investigation of neopentylglycol $(CH_3)_2C(CH_2OH)_2$ and pentaglycerol $CH_3C(CH_2OH)_3$ in order to elucidate the molecular structure and hydrogen bonds in the crystal and to make a comparison with pentaerythritol $C(CH_2OH)_4$.[1-4]

For pentaglycerol, three-dimensional intensity data were collected by the photographic method. In these photographs, diffuse scatterings are observed in addition to Bragg reflections. If we disregard the diffuse scatterings, the photographs show the same space group and almost the same cell size and intensity distribution as pentaerythritol. This indicates that the crystal structure is similar to that of pentaerythritol. In the crystal of pentaerythritol, each molecule is required by space-group symmetry to be located at the special position of a unit cell with the molecular symmetry of $\bar{4}$. In the case of pentaglycerol, on the other hand, the molecule can not have such a high symmetry, since only three CH_2OH groups exist in a molecule. Thus, it would be necessary to assume some disordered arrangement of molecules in the crystal of pentaglycerol. A more detailed analysis of the structure is now in progress.

The crystal structure of neopentylglycol was established; it will be mentioned below. Specimens suitable for X-ray work were obtained from the benzene solution in the form of colorless needles elongated along the *a* axis. The crystals are monoclinic, with four molecules in a unit cell with the dimensions of $a=6.01$, $b=10.91$, $c=10.18$ Å, and $\beta=100.0°$. The space group was found to be $P2_1/n$. The density calculated was $1.05\ g\cdot cm^{-3}$. Since the crystal was fairly volatile, samples were sealed into glass capillaries. Weissenberg intensity data were collected by means of Cu$K\alpha$ radiation on the *a* axis for from zero to the fourth layer, and on the *c* axis for from zero to the fifth layer. 808 reflections were observed; 105 were too weak to be measured.

From the three-dimensional sharpened Patterson function, molecular orientation and intermolecular O- - -O (the hydrogen bond) vectors were established by interpreting vectors from 2.4 to 3.0 Å around the point of origin. Using the 0kl data, an approximate structure was obtained by the trial method, the molecular orientation being taken into consideration. Refinements were carried out by means of a block-diagonal least-squares method, and the discrepancy index, R was reduced to 18.5%, excluding unobserved reflections.

The partial structure–$C(CH_2OH)_2$ group in neopentylglycol is the same as that in pentaerythritol. The average bond distance is 1.56 Å for C–C and 1.45 Å for C–O. The average bond angle is 109.5° for C–C–C and 110.9° for C–C–O. The mode of packing of the molecules in the crystal and the electron density can be seen in Fig. 1. Two intermolecular separations, O(1)- - -O(2) of 2.65 Å and O(1)- - -O(2) of 2.72 Å, correspond to hydrogen bonds which link the molecules in infinite ribbons along the *a* axis. It is also interesting that the arrangement of four hydrogen bonds around the center of symmetry is similar to that of pentaerythritol. A detailed account of this work will be published in the near future.

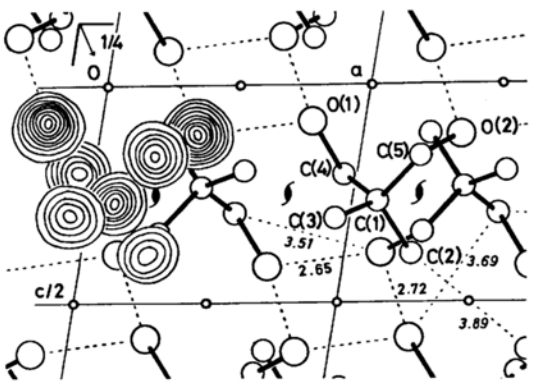

Fig. 1. Arrangement of the molecules along the *b* axis.

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