
LETTER

X-Ray Investigation of Trimethylacetic Acid Crystal

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Timmermans⁽¹⁾ elucidated that trimethylacetic acid (pivalic acid) crystal possesses a very small entropy of fusion, 2.6 e. u./mole, and is an example of the organic plastic crystals so called by him. Hence, we have now carried out an X-ray investigation of this crystal in order to amplify our knowledge on the structures of such plastic crystals as cubic pentaery-

thritol,⁽²⁾ tetranitromethane,⁽³⁾ cyclohexane,⁽⁴⁾ cyclohexanol⁽⁵⁾ and hexachloroethane.⁽⁶⁾

The present material was prepared by the method of Puntambeker and Zoellner⁽⁷⁾ and the product was subjected to fractional recrystallization and distillation, m. p. 33–34°. Samples of this compound were sealed in thin-walled glass capillary tubes and the single crystals were grown from the liquid by slow cooling of the tubes previously warmed to 40°. Rotation and oscillation photographs were obtained with these crystals using Cu

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radiations. From the results it was found that the crystal conforms to a face-centered cubic lattice, containing four molecules of $(\text{CH}_3)_3\text{CCO}_2\text{H}$ in the unit cell with the edge $a=8.82$ Å. The calculated density is 0.98, which is 'reasonable in comparison with values extrapolated from the known⁽⁸⁾ densities of the liquid. The space group is $T^2-F\bar{2}3$, $T^2_8-Fm\bar{3}$, $T^2_8-F\bar{4}3m$, $O^3-F\bar{4}3$ or most probably $O^5_8-Fm\bar{3}m$. From the symmetry consideration it is shown that the molecules arranged at 0, 0, 0; 0, 1/2, 1/2; 1/2, 0, 1/2; 1/2, 1/2, 0 take either orientational or rotational disorder.

Such structure is seen to be in harmony with the extraordinarily rapid decrease of the intensities for increasing angle of scattering. On the other side, on several Laue photographs there appeared intense diffuse spots such as accompanied by {111} and {200}. These results are quite in resemblance to certain cases^{(2),(4),(5)} of the above examples and those of *t*-butyl chloride, *t*-butyl bromide and neohexane recently published by Schwartz, Post and Fankuchen.⁽⁹⁾

It may be added that we have confirmed optically that the isotropic⁽⁸⁾ crystals transform at about -2° to small birefringent needles. The transition may be due to cessation of the molecular rotation.

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