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Kurze Originalmitteilungen

X-ray Analysis of the Structure of Harman, $C_{12}H_{10}N_2$.

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(Received April 19, 1958)

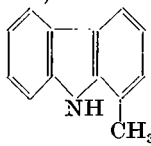
Auszug

Aus Röntgenaufnahmen folgt, daß die Kristalle von Harman der rhombischen Raumgruppe $P2_12_12_1$ angehören und 8 Moleküle $C_{12}H_{10}N_2$ in der Elementarzelle mit den Gitterkonstanten $a = 9{,}6$ Å, $b = 13{,}6$ Å, $c = 15{,}6$ Å enthalten. Die Hauptbrechungsindizes sind $n_\alpha = 1{,}711$, $n_\beta = 1{,}731$ und $n_\gamma = 1{,}749$.

Abstract

X-ray and optical measurements show the orthorhombic nature of the crystals of harman, $C_{12}H_{10}N_2$, having the unit-cell dimensions $a = 9.6$ Å, $b = 13.6$ Å and $c = 15.6$ Å with the principal refractive indices $\alpha = 1.711$, $\beta = 1.731$ and $\gamma = 1.749$. The systematic absence observed leads to the space-group $P2_12_12_1$ and the density determination suggests 8 molecules of harman in the unit-cell of the given dimensions.

Preliminary results of the structure of the heterogeneous ring compound nor-harman, $C_{11}H_8N_2$, prior to the determination of the atomic configuration have already been reported[1]. The compound nor-harman and harman have the same structural formula except for the methyl-pyridine ring in the latter. Harman has been analysed in the present case to see whether the assumptions made in the FOURIER synthesis of the structure of nor-harman can justiably be applied in the present synthesis.

Harman, a colourless compound melting at 237—238 °C has the structural formula  N. Crystallization of the substance (Pfizer products with melting point 237 °C) from a solution in a mixture of alcohol and benzene gave stout tablet like crystals. Elongated needle like crystals were obtained from only a single crop crystallized from the synthetic products very kindly supplied by Dr. (Mrs.) A. CHATTERJEE. On subsequent re-crystallization of the synthetic products no such crystals were obtained, only tablet like crystals as from the Pfizer products were obtained.

[1] LILABATI RAY, Preliminary single-crystal X-ray and optical study of nor-harman, $C_{11}H_9N_2$. Acta Crystallogr. **10** (1957) 707.

A thorough optical examination has been carried out by a polarizing microscope. The crystals were found to be anisotropic and exhibit an orthorhombic symmetry. The crystals show a positive bi-refringence with the optic directions X and Y parallel to the a- and b-crystallographic directions and the Z direction perpendicular to the ab-plane. The refractive indices along the three crystallographic directions measured by BECKE's method were found to be:

$$n_\alpha\,(//a) = 1.711, \quad n_\beta\,(//b) = 1.731 \text{ and } n_\gamma\,(//c) = 1.749.$$

Over-exposed rotation diagrams were taken about the three principal crystallographic directions with very thin clear single crystals grown from both the Pfizer and the synthetic products. The axial lengths calculated from the spacings of the higher order layer lines of the rotation diagram gave the following values:

$$a = 9.6 \text{ Å}, \quad b = 13.6 \text{ Å and } c = 15.6 \text{ Å}.$$

Photographs of the different reciprocal lattice layers were taken by the normal and the equi-inclination moving film technique. On indexing the reflection planes from the WEISSENBERG photographs by the conventional method the following systematic abscences were obtained:

Only odd orders of $(h00)$, $(0k0)$ and $(00l)$ planes were absent suggesting the three two-fold screw axis; no systematic absences were observed for the other types of planes. These systematic reflection conditions lead to the space-group $P2_12_12_1$ with four molecules of harman in each unit-cell. The density of the crystal determined by the floatation method was found to be 1.203 g/cm^3. Hence the number of harman molecules in the elementary cell of the given dimensions come out to be 8. But the space-group and the symmetry condition permits only four equivalent positions. Hence it is very likely that either the molecules are at the eight general positions or two molecules of harman forming a single group are at each of the four special positions; of course the orientation of the molecules within each group cannot be definitely said at this stage.

In order to arrive at a correct model of the structure, the molecule is assumed to be planar and it was found that the observed intensity of reflection can be better explained on a planar model.

Several facts such as the length of the molecule and the dimensions of the unit-cell suggest that the molecules are lying with their lengths essentially parallel to the c-axis. The strong (110) reflection further confirms this idea. The nearly isotropic optical character further suggests that the plane of the molecule is inclined in all directions.

The relative intensities of the planes were found to be in reasonable agreement with those calculated on the above mentioned structural model.

The shape and size of the harman molecule is rather uncertain, but from a study of a number of organic compounds of similar order of complexity it seems very likely that the assumptions made above are near the true state of affairs. Further work on the synthesis of the structure is in progress.

The authors wishes to acknowledge their indebtedness to Prof. S. N. Bose for his constructive criticism and helpful discussions during the progress of the work. Thanks are also due to Dr. (Mrs.) A. Chatterjee of the Department of Organic Chemistry, Calcutta University, for kindly preparing the sample. Thanks are also due to Dr. F. A. Hochstein of Chas. Pfizer & Co. INC., of Brooklyn for kindly supplying the sample.

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Correction to paper by Y. Takeuchi and R. Pepinsky

The Crystal Structure of Pyridinium Reineckate

By R. Pepinsky

(Received May 30, 1958)

W. Nowacki has kindly pointed out an error in indexing of our ($hk0$) X-ray data for the structure analysis of pyridinium reineckate[1]. In the ($hk0$) indexing shown in our Table 2, all values of k should be *doubled.* In addition, (040) should read (060), and (050) should read (080).

In preparing data for X-RAC computation, if one index is always *even* we often use the halved value of the even index. This was done for the present ($hk0$) projection; but then the k values were not doubled, as they should have been, in the tabulation.

The indices are otherwise correct, and all coordinates and the space group ($A\ 2/a$) are correctly given.

We are grateful to Prof. Nowacki for pointing out the discrepancy to us.

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[1] Y. Takeuchi and R. Pepinsky, Z. Kristallogr. **109** (1957) 29—41.

The International Union of Crystallography

X-ray Powder Data File

Upon the resignation of Dr. G. W. Brindley, Dr. J. V. Smith has been appointed acting Editor to the X-ray Powder Data File. New data and information concerning errors in the published data are always welcome and correspondence should be addressed to Dr. J. V. Smith, Mineral Science Building, The Pennsylvania State University, University Park, Pennsylvania, U. S. A.