factory result when applied to V_3Au, it does not do so for many other compounds.

(3) Finally, are the new results, judged simply as an empirical correlation, an improvement on those of this author? The mean deviation in lattice constant obtained by the author for the 32 compounds is 0·01 Å, the range is 0·00–0·03 Å; for 31 compounds it is 0·00–0·02 Å. In this case, therefore, the mean deviation may be given as a meaningful measure of agreement. It was pointed out (Geller, 1956) that the accuracy of the measured lattice constants would not seem to warrant an attempt to obtain better agreement of predicted with measured lattice constants. Pauling has obtained a mean deviation in lattice constant of 0·004 Å. However, the range is 0·000–0·030 Å. Four of the deviations are greater than or equal to five times the mean deviation. Thus, the accuracy claimed by Pauling is illusory, and the results are really no better than those originally obtained by the author.

It is therefore necessary to conclude in answer to the three questions put at the introduction (1) that Pauling has not demonstrated that the resonating-valence-bond theory applies to the compounds with the β-W structure; (2) that the technique used to obtain his β-W radii is new and has not been justified in detail; (3) that the new results are no better than those of this author. The latter have the advantages that (1) they adhere to the generally accepted idea of simple additivity of radii for prediction of interatomic distances, and (2) they recognize the shortcomings of the experimental data.

References

GELLER, S. (1956). *Acta Cryst.* **9**, 885.

MATTHIAS, B. T., WOOD, E. A., CORENZWIT, E. & BALA, V. B. (1956). *J. Phys. Chem. Solids.* **1**, 188.

PAULING, L. (1945). *The Nature of the Chemical Bond.* Ithaca: Cornell University Press.

PAULING, L. (1947). *J. Amer. Chem. Soc.* **69**, 542.

PAULING, L. (1957). *Acta Cryst.* **10**, 374.

Acta Cryst. (1957). 10, 382

Some pyridine-*N*-oxide derivatives.*

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A survey was undertaken some months ago of pyridine-*N*-oxide derivatives with a view to obtaining cell data of crystalline specimens to aid in a diligent choice of compounds for complete X-ray analysis. Two such compounds have meantime been so analyzed to furnish bond data for theoretical chemists (Eichhorn, 1956, 1957; Jaffe & Doak, 1955).

Table 1 reproduces the data of the eight crystalline compounds investigated. The authors have to thank Dr H. J. den Hertog of the Wageningen Agricultural Institute and Dr E. Ochiai of the University of Tôkyo for the many samples placed at their disposal. The carbinol was first prepared by synthesis at C.I.T. by Dr R. L. Bixler, who was good enough to let us have a sufficient quantity for our experiments. Great difficulties were initially experienced with the purification of this compound since it would not properly dissolve in many of the commonly used organic solvents. With dioxane, however, the carbinol combines to give a molecular compound of uncertain dioxane content, yielding beautiful silky needles which will lose dioxane after some standing; the needles finally revert to powder.

Table 1. *Crystallographic data*

d_f and d_x are the densities, measured respectively by flotation (usually with the aid of an electrically driven centrifuge) and determined by calculation from the molecular weight and the cell volume. The translation distances were determined from oscillation photographs (Cu $K\alpha$ = 1·5418 Å), and their precision should be of the order of 0·02 Å. The axial angles should have a precision of about 0·1°; the d_f value for the last compound in the table is not very reliable.

4-Nitro-P*N*O

Pmna; $Z = 4$; $d_f = 1{\cdot}520$, $d_x = 1{\cdot}550$ g.cm.$^{-3}$
$a = 12{\cdot}53$, $b = 6{\cdot}04$, $c = 7{\cdot}93$ Å

4-Chloro-P*N*O

Fddd; $Z = 16$; $d_f = 1{\cdot}444$, $d_x = 1{\cdot}440$ g.cm.$^{-3}$
$a = 19{\cdot}69$, $b = 12{\cdot}87$, $c = 9{\cdot}54$ Å

4-Cyano-P*N*O

$P2_1/c$; $Z=4$ with sub-cell $c' = \frac{1}{2}c$; $d_f = 1{\cdot}355$, $d_x = 1{\cdot}360$ g.cm.$^{-3}$
$a \sin\beta = 11{\cdot}31$, $b = 5{\cdot}90$, $c = 7{\cdot}89$ Å

4,4′-*trans*-Azo-P*N*O

$P2_1/n$; $Z = 2$; $d_f = 1{\cdot}497$, $d_x = 1{\cdot}504$ g.cm.$^{-3}$
$a = 4{\cdot}56$, $b = 12{\cdot}75$, $c = 9{\cdot}75$ Å, $\beta = 114{\cdot}6°$

4,4′-*cis*-Azo-P*N*O

$P2_1/a$; $Z = 4$; d_f = ?, $d_x = 1{\cdot}237$ g.cm.$^{-3}$
$a = 15{\cdot}44$, $b = 22{\cdot}01$, $c = 3{\cdot}76$ Å, $\beta = 114{\cdot}9°$

4-Hydroxy-P*N*O

$P1$ or $P\bar{1}$; $Z = 2$; $d_f = 1{\cdot}536$, $d_x = 1{\cdot}541$ g.cm.$^{-3}$
$a=3{\cdot}85$, $b=7{\cdot}10$, $c=13{\cdot}10$ Å, $\alpha=116{\cdot}5°$, $\beta=121{\cdot}0°$, $\gamma=93{\cdot}7°$

4-Pyridyl-*N*O-carbinol

$P2_1/c$; $Z = 4$; d_f = ?, $d_x = 1{\cdot}233$ g.cm.$^{-3}$
$a = 13{\cdot}89$, $b = 3{\cdot}93$, $c = 12{\cdot}33$ Å, $\beta = 90{\cdot}0°$

X Dioxane. *Y* 4-pyridyl-*N*O-carbinol

$P2_1/c$; Z = ?; $d_f = 1{\cdot}11$, d_x = ? g.cm.$^{-3}$
$a = 7{\cdot}58$, $b = 5{\cdot}95$, $c \sin\beta = 12{\cdot}74$ Å

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References

EICHHORN, E. L. (1956). *Acta Cryst.* **9**, 787.

EICHHORN, E. L. (1957). To be published.

JAFFE, H. H. & DOAK, G. O. (1955). *J. Amer. Chem. Soc.* **77**, 4441.

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