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Crystallographic properties of 4-picoline-N-oxide.

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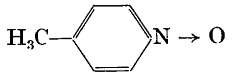
The compound 4-picoline-N-oxide is represented by the following formula:



Crystallization from benzene–petroleum ether solution gives tetragonal bipyramids showing the 101 faces. The sample used for the powder pattern melted in the range of 183·5–185·0 °C. The crystal system is tetragonal with 8 molecules of C_6H_7NO per cell. The observed density is 1·168 g.cm.$^{-3}$ (displacement) while the density calculated from X-ray data is 1·132 g.cm.$^{-3}$

$$a = b = 8{\cdot}04,\ c = 19{\cdot}84\ \text{Å}\ .$$

The space group, based on the observed systematic extinctions is C_4^6–$I4_1$. If this assignment is correct, the crystal is the first found in this space group (Donnay & Nowacki, 1954).

The optical properties are:

$$E > 1{\cdot}70,\ W = 1{\cdot}504,\ \text{optic sign}\ +.$$

The powder data (Table 1) were obtained using a camera 114·6 mm. in diameter with copper radiation and nickel filter. The indexing was done on the basis of *a* axis and *c* axis single crystal rotation patterns. Other Miller indices can be found having the same interplanar spacing values; however, based on the single crystal data, only those named were of strong enough intensity to contribute significantly to the intensity of the line.

Table 1. *X-ray powder diffraction data for 4-picoline-N-oxide*

d_o (Å)	I/I_1	*hkl*	d_c (Å)
7·49	0·12	101	7·45
4·94	1·00	112	4·93
4·02	1·00	200	4·02
3·54	0·16	211	3·54
3·14	0·20*b*	213, 204	3·16, 3·12
2·83	0·12	220	2·84
2·65	0·16	301	2·66
2·46	0·16	224	2·46
2·21	0·08	305, 321	2·22, 2·22
2·11	0·02	323	2·11
2·01	0·08	316, 400	2·02, 2·01
1·938	0·02	325	1·944
1·867	0·16	—	—
1·794	0·02	—	—
1·752	0·02	—	—
1·685	0·04	—	—
1·643	0·02	—	—
1·557	0·02	—	—
1·489	0·02	—	—
1·362	0·02	—	—
1·318	0·02	—	—
1·253	0·02	—	—
1·232	0·02	—	—

Reference

Donnay, J. D. H. & Nowacki, W. (1954). *Crystal Data.* The Geographical Society of America, New York, U.S.A.

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Elementarzellen und Raumgruppen der cyclischen Urethan-Oligomeren 1,8-Diaza-10,15-dioxa-9,16-dioxo-cyclohexadecan und 1,8,17,24-Tetraaza-10,15,26,31-tetraoxa-9,16,25,32-tetraoxo-cyclo-duotriakontan.*

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Aus einem technischen Polyadditionsprodukt aus Butandiol-(1,4) und Hexandiisocyanat-(1,6) isolierten Zahn & Dominik (1960, 1961) das monomere (I) und dimere (II) cyclische Oligomere:

$$\overline{\llcorner[\mathrm{OC.NH(CH_2)_6NH.CO.O(CH_2)_4.O}]_n\lrcorner}$$

$$\text{I: } n = 1,\ \text{II: } n = 2\ .$$

Die monomere Verbindung (I) kristallisierte aus Methanol in rhombischen Blättchen. Blättchenebene (100). Drehkristallaufnahmen ergaben eine orthorhombische Elementarzelle mit den Translationsperioden:

$$a_0 = 17{,}38 \pm 0{,}04,\ b_0 = 8{,}95 \pm 0{,}07,\ c_0 = 17{,}86 \pm 0{,}1\ \text{Å};$$
$$\alpha = \beta = \gamma = 90°.$$

Bei Annahme von 8 Molekülen in der Elementarzelle wird die Dichte zu 1,235 g.cm.$^{-3}$ berechnet (bei 24–28 °C.). Am Kristallpulver wurden gemessen: 1,241 g.cm.$^{-3}$ (21 °C.). Kombinierte Weissenberg- und Präzessionsaufnahmen nach Buerger um die *c*-Achse ergaben einen Ausschnitt aus dem reziproken Gitter. Die fehlenden Reflexe *hkl* mit $h + k = 2n + 1$ zeigten eine *C*-Zentrierung an. Unter den verbleibenden Möglichkeiten konnte auf Grund der fehlenden Reflexe *h0l* mit $l = 2n + 1$ zugunsten der Raumgruppe *Cmcm* entschieden werden.

Die dimere Verbindung (II) wurde im Einschlussrohr aus Methanol in monoklinen Blättchen erhalten. Aus-

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* 24. Mitteilung über Oligomere; 23. Mitt. vgl. H. Zahn & M. Dominik, *Makromolekulare Chem.* 1961, **44-46**, 290.

gebildet waren ausschliesslich (100)-Flächen (Blättchenebene) und (011)-Flächen.

Die Elementarzelle besitzt die Abmessungen:

$$a_0 = 16{,}45 \pm 0{,}02,\; b_0 = 9{,}93 \pm 0{,}035,\; c_0 = 9{,}49 \pm 0{,}02 \text{ Å};\quad \beta = 107{,}9 \pm 0{,}2°;\; \alpha = \gamma = 90°.$$

Nimmt man an, dass 2 Moleküle in der Zelle enthalten sind, ergibt eine Berechnung der Dichte 1,163 g.cm.$^{-3}$.

Gemessen: 1,16$_5$ g.cm.$^{-3}$.

Ein Ausschnitt aus dem reziproken Gitter wurde in gleicher Weise wie bei der monomeren Verbindung gewonnen. Es wurde um die ausgezeichnete Achse (b-Achse) gedreht und präzessiert. Allgemeine Auslöschungen (hkl) traten nicht auf. Die fehlenden Reflexe $h0l$ mit $l = 2n + 1$ und $0k0$ mit $k = 2n + 1$ weisen der Verbindung die Raumgruppe $P2_1/c$ zu.

Ich danke dem Bundeswirtschaftsministerium (Forschungsvorhaben J 272) für die Unterstützung dieser Arbeit. Herrn Prof. Dr. Wölfel, Technische Hochschule Darmstadt, danke ich für die Hilfe bei der Gewinnung der Präzessionsaufnahmen der monomeren Verbindung. Mein Dank gilt weiterhin Herrn Prof. Dr. Zahn für die Anregung der Arbeit und Dr. Dominik für die Überlassung der Oligomeren.

References

Zahn, H. & Dominik, M. (1960). *Ang. Chem.* **72**, 273.
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Coordinate errors due to rotational oscillations of molecules.

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The writer has shown (Cruickshank, 1956*a*) how molecular angular oscillations can cause the maximum of an atomic peak in the electron density to be displaced towards the centre of rotation. The shift was taken to be in a radial direction and was calculated as

$$\Delta = \tfrac{1}{2} r \left(\frac{s^2}{1 + s^2/q^2} + \frac{t^2}{1 + t^2/q^2} \right) , \tag{1}$$

where r is the distance from the centre of molecular oscillation, s^2 and t^2 are the mean square amplitudes of oscillation of the atom in the rotations about the two principal axes perpendicular to the radius and q^2 is the Gaussian-breadth parameter for the peak before the rotational oscillations are considered. The previous derivation assumed that only angular oscillations about axes perpendicular to the radius were relevant, since the atom is not moved by an oscillation about this radius. This assumption is clearly wrong in general. For if there is an atom at $(x, y, 0)$ and all the elements of the ω_{ij} angular oscillation tensor (Cruickshank, 1956*b*) are zero except ω_{11}, the shift will obviously be towards the x-axis and not towards the origin, so that the maximum will appear at $(x, y - \Delta', 0)$ and not at $\{x(1 - \Delta/r), y(1 - \Delta/r), 0\}$. Equation (1) evidently gives the total shift only when a principal axis of ω_{ij} coincides with the radius to the atom.

The previous formula was derived by finding the maximum of the electron density along the radius. The general problem is more difficult since the direction of the shift is unknown. An approximate formula is derived below from a centre-of-gravity approach.

Let $\mathbf{r} = (x, y, z)$ be the equilibrium position of an atom and $\boldsymbol{\varphi} = (\varphi_1, \varphi_2, \varphi_3)$ be an arbitrary small rotation of the molecule. Then the combined effect of rotations by $\boldsymbol{\varphi}$ and $-\boldsymbol{\varphi}$ will be to produce a weighted contribution to the total electron density whose maximum will lie on the normal

$$\mathbf{a} = -\mathbf{r} + (\mathbf{r} \cdot \boldsymbol{\varphi}/\varphi^2)\boldsymbol{\varphi} \tag{2}$$

from the atom to the axis of oscillation and which will be displaced from the equilibrium position by the small amount $\frac{1}{2}\mathbf{a}\varphi^2$. The x component of this displacement is

$$\Delta_x(\boldsymbol{\varphi}) = -\tfrac{1}{2} x(\varphi_2^2 + \varphi_3^2) + \tfrac{1}{2} y\varphi_1\varphi_3 + \tfrac{1}{2} z\varphi_1\varphi_2 \,. \tag{3}$$

It is shown in the Appendix that the weight to be associated with the contribution at this point is approximately $P(\boldsymbol{\varphi})D(a\varphi)$, where $P(\boldsymbol{\varphi})$ is the probability of an oscillation $\boldsymbol{\varphi}$ and $D(a\varphi)$ is the density of the original Gaussian peak at a distance $a\varphi$ from its centre. The values of $P(\boldsymbol{\varphi})$ and $D(a\varphi)$ are proportional to

$$P(\boldsymbol{\varphi}) = \exp\left(-\tfrac{1}{2}\Sigma\Sigma\omega^{-1}{}_{ij}\varphi_i\varphi_j\right) , \tag{4}$$

and

$$D(a\varphi) = \exp\left(-\tfrac{1}{2}a^2\varphi^2/q^2\right) , \tag{5}$$

where $\omega^{-1}{}_{ij}$ is an element of the matrix inverse to ω_{ij}, defined with respect to the arbitrary x, y, z axes, and the summations are for $i, j = 1, 2, 3$.

Thus the x component of the net shift due to the whole angular oscillation specified by ω_{ij} is

$$\varepsilon_x = \int \Delta_x(\boldsymbol{\varphi})P(\boldsymbol{\varphi})D(a\varphi)d\boldsymbol{\varphi} \Big/ \int P(\boldsymbol{\varphi})D(a\varphi)d\boldsymbol{\varphi} \,. \tag{6}$$

Using (2) we can write

$$P(\boldsymbol{\varphi})D(a\varphi) = \exp\left(-\tfrac{1}{2}\Sigma\Sigma A_{ij}\varphi_i\varphi_j\right) , \tag{7}$$

where

$$\left.\begin{aligned} A_{11} &= (y^2 + z^2)/q^2 + \omega^{-1}{}_{11} , \\ A_{12} &= -xy/q^2 + \omega^{-1}{}_{12}, \text{ etc.} \end{aligned}\right\} \tag{8}$$

Since $\Delta_x(\boldsymbol{\varphi})$ is given by (3), we need the result that

$$\begin{aligned} &\int \varphi_i\varphi_j \exp\left(-\tfrac{1}{2}\Sigma\Sigma A_{ij}\varphi_i\varphi_j\right)d\boldsymbol{\varphi} \\ &= A^{-1}{}_{ij} \int \exp\left(-\tfrac{1}{2}\Sigma\Sigma A_{ij}\varphi_i\varphi_j\right)d\boldsymbol{\varphi} , \end{aligned} \tag{9}$$

where $A^{-1}{}_{ij}$ is an element of the matrix inverse to A_{ij}. By combining (3), (7) and (9) with (6) the net shift of the electron-density maximum can be found. Reversing