axes one of which (of *minimum* translation) is *in* the molecular plane and *along* a chain of molecules linked by H-bonds, the other two being inclined at 9·3° and −80·7° to the molecular normal. The librational vibrations are perhaps more likely to be closely related to the molecular geometry (axes of inertia); and the intramolecular vibrations certainly will be. Except in the case of highly-symmetrical crystals containing highly-symmetrical molecules, therefore, the resultant thermal ellipsoids probably will be orientated so that principal axes lie *between* those which would refer ω to the principal molecular axes and those corresponding with translation directions towards nearest parallel molecules. Since, in aromatic compounds, the molecular planes often make angles of about ±30° or less with one crystal plane (thus forming a pseudo-layer structure), the deviations of one of the three sets of B_{ij} directions from the molecular normal is not likely to be large (possibly about 15° or less), but it is important that this deviation should be recognized as real.

3. Alternative methods of determining B_{ij} directions

As has been mentioned earlier, Fourier sections and projections (especially difference syntheses) will often indicate atomic ellipsoid orientations. Whether these are likely to be more accurate than those deduced from the b_{ij} is a matter to be decided only by experience. Alternatively, determination of the Debye factors directly from the experimental data for two or three informed guesses at the atomic principal axis directions, thus 'sampling' the atomic vibration ellipsoids in various ways, may possibly give more reliable thermal information than the determination and subsequent conversion of b_{ij} values.

Certainly it is *not* safe to rely upon one determination only of a set of b_{ij} deduced from experimental data at one temperature, even for *R*-values as low as 0·05, unless the e.s.d. are smaller by an order of magnitude than those now usually accepted as reasonable.

Finally we would beg crystallographers not to mislead interested research workers in other disciplines by giving b_{ij} or B_{ij} values to 4 or 5 apparently significant figures (without proper qualification), unless and until they have repeated their measurements and refinements more than once, independently, and have proved experimentally that a claim to such accuracy is justified.

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The crystal structure of azodicarbonamide. By JOHN H. BRYDEN,* *Chemistry Division, Research Department, U.S. Naval Ordnance Test Station, China Lake, California, U.S.A.*

Azodicarbonamide, $H_2N–CO–N=N–CO–NH_2$, is prepared by the oxidation of hydrazodicarbonamide in a potassium dichromate-sulfuric acid solution (Thiele, 1892). Hydrazodicarbonamide is obtained by the reaction of hydrazine sulfate and potassium cyanate (Thiele, 1892). Azodicarbonamide is insoluble in most common organic solvents and is only slightly soluble in water. Crystals were grown by slow cooling of a hot aqueous solution. They were found to be monoclinic with elongation in the direction of the *a* axis and showing the forms {011} and {101}. The crystals cleaved easily parallel to (101). Many of the crystals were double crystals by twinning on (001). This occurred in such a manner that the positive direction of the *a* axis was oppositely directed in the two parts.

The following unit-cell dimensions were obtained from

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rotation and Weissenberg photographs taken about the *a* and *b* axes (λ of Cu $K\alpha = 1·5418$ Å):

$$a_0 = 3·57 \pm 0·01, \quad b_0 = 9·06 \pm 0·02, \quad c_0 = 7·00 \pm 0·02 \text{ Å};$$
$$\beta = 94° 50' \pm 15'.$$

The extinctions observed (*hkl* present in all orders, *h0l* present only with $h+l=2n$, and $0k0$ present only with $k=2n$) uniquely determined the space group as $P2_1/n$. The calculated density for two centrosymmetric molecules of $C_2H_4N_4O_2$ per unit cell is 1·708 g.cm.$^{-3}$.

The intensity data for the structure determination were estimated visually from multiple-film equi-inclination Weissenberg photographs of the $0kl$ and $1kl$ reflections. Initial parameters of the projected structure were obtained easily from the sharpened $0kl$ Patterson projection by use of a reasonable model of the molecule. This initial arrangement was refined by least-squares and

Table 1. *Final results based on the $1kl$ data*

Atom	x	y	z	ϱ_0 (e.Å^{-2})	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)	$\lvert\partial^2\varrho/\partial y^2\rvert$ (e.Å^{-4})	$\lvert\partial^2\varrho/\partial z^2\rvert$ (e.Å^{-4})
O	$-0\cdot282$	$0\cdot0932$	$0\cdot2814$	$9\cdot73$	$0\cdot019$	$0\cdot009$	$0\cdot012$	$101\cdot2$	$84\cdot9$
N_1	$0\cdot054$	$0\cdot0648$	$-0\cdot0022$	$8\cdot28$	$0\cdot022$	$0\cdot010$	$0\cdot014$	$87\cdot9$	$73\cdot8$
N_2	$-0\cdot082$	$0\cdot2927$	$0\cdot1190$	$8\cdot31$	$0\cdot022$	$0\cdot012$	$0\cdot014$	$81\cdot5$	$74\cdot6$
C	$-0\cdot122$	$0\cdot1520$	$0\cdot1460$	$6\cdot74$	$0\cdot027$	$0\cdot013$	$0\cdot015$	$68\cdot1$	$70\cdot3$

$$\sigma(A_k) = 0\cdot912 \text{ e.Å}^{-3}. \qquad \sigma(A_l) = 1\cdot039 \text{ e.Å}^{-3}. \qquad \sigma(\varrho) = 0\cdot319 \text{ e.Å}^{-2}.$$

Fourier methods. The final Fourier projection is shown in Fig. 1. The final percentage discrepancy for the $0kl$ structure amplitudes, calculated with parameters from the $0kl$ data only, was $13\cdot2$. An isotropic temperature correction, $\exp[-B(\sin\theta/\lambda)^2]$, with $B = 4\cdot67$ Å^2, and scattering factors calculated by the equation described by Vand, Eiland & Pepinsky (1957) were used in calculating the structure amplitudes. The constants for the scattering factor equation were obtained from the scattering factor data given by Hoerni & Ibers (1954).
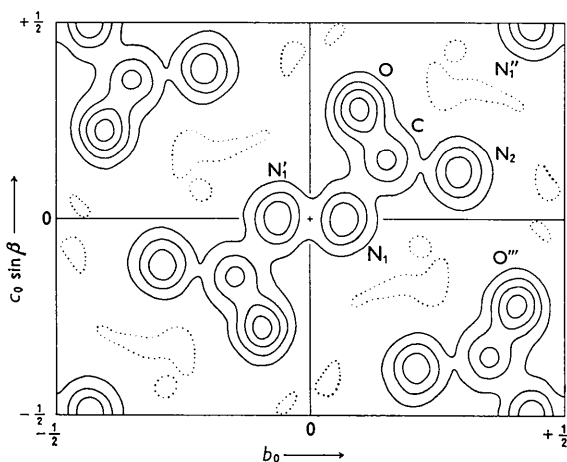

Fig. 1. Fourier projection of azodicarbonamide on (100). Contour interval is 2 e.Å^{-2}. The zero contour is dotted.

The complete crystal structure was obtained from the 148 observed $1kl$ reflections. The $0kl$ data were not used in this stage of the structure analysis. The great intensity of the (101) reflection suggested that the molecule was nearly parallel to this plane. Initial values of the x parameters were obtained by this assumption. All parameters were then refined by generalized Fourier projections, using the method described by Fridrichsons & Mathieson (1955). The final parameters, corrected for series termination errors by the method of Booth (1946), are listed in Table 1, together with their standard deviations and the heights and curvatures of the atom peaks. The standard deviations of the y and z parameters were obtained from the modulus projection by the procedure of Cruickshank (1949). Those of the x parameters were calculated from the modulus projection by the equation

$$\sigma(x_i) = (a_0/2\pi h)\,.\,\sigma(\varrho)/\varrho_i\,,$$

where $\sigma(\varrho)$ is the standard deviation of the electron density (Cruickshank, 1949) and ϱ_i is the height of the ith atomic peak. The final percentage discrepancy for the $1kl$ structure amplitudes was $20\cdot2$. Again an isotropic temperature correction with $B = 2\cdot93$ Å^2 and the scatter-

ing factor equation of Vand, Eiland & Pepinsky (1957) were used. The poorer agreement found for the $1kl$ data as compared with the $0kl$ data is probably due to the inferior quality of the crystals used to obtain the $1kl$ photographs. Untwinned crystals were invariably hollow.

Table 2 lists important interatomic distances and bond angles. The azo bond length of $1\cdot24$ Å agrees, within the experimental error, with the value of $1\cdot23$ Å found in the *trans* and *cis* azobenzenes (de Lange, Robertson & Woodward, 1939; Hampson & Robertson, 1941), and with the value of $1\cdot26$ Å found in azo-*bis*-N-chloroformamidine (Bryden, 1958). The C–N$_1$ distance of $1\cdot48$ Å corresponds to a carbon–nitrogen single bond. The other bond lengths correspond to urea-type resonance (Vaughan & Donohue, 1952) with the carbon–oxygen and carbon–nitrogen bonds having 45% and 55% double bond character respectively. The four atoms making up half of the chemical molecule are planar to within the accuracy of the structure analysis, the average deviation from the least-squares plane being $0\cdot003$ Å (maximum of $0\cdot006$ Å for the carbon atom). However, the perpendicular distance of this plane from the origin is $0\cdot144$ Å, indicating a slight rotation about the C–N$_1$ bond.

Table 2. *Interatomic distances, standard deviations of bond lengths, and bond angles*

	(Å)	(Å)		(°)
N_1–N_1'	$1\cdot24$	$0\cdot031$	C–N_1–N_1'	$109\cdot5$
C–N_1	$1\cdot48$	$0\cdot024$	O–C–N_1	$123\cdot0$
C–O	$1\cdot27$	$0\cdot023$	O–C–N_2	$125\cdot7$
C–N_2	$1\cdot30$	$0\cdot018$	N_1–C–N_2	$111\cdot3$
$N_2\cdots N_1''$	$3\cdot31$	$0\cdot022$	C–$N_2\cdots N_1''$	$102\cdot2$
$N_2\cdots O'''$	$2\cdot87$	$0\cdot021$	C–$N_2\cdots O'''$	$121\cdot8$
			$N_1''\cdots N_2\cdots O'''$	$136\cdot0$

Two possibilities of hydrogen bonding exist: a nitrogen–oxygen hydrogen bond between N_2 and O''' of length $2\cdot87$ Å, and a nitrogen–nitrogen hydrogen bond between N_2 and N_1'' of length $3\cdot31$ Å. The oxygen atom is $0\cdot31$ Å and N_1'' is $0\cdot24$ Å out of the plane of the half-molecule containing N_2. Therefore, both O''' and N_1'' are well situated geometrically to form good hydrogen bonds. Each molecule is hydrogen bonded to four surrounding molecules in the same plane, thus forming sheets which are nearly parallel to the (101) plane. The forces holding these sheets together are of the van der Waals' type as evidenced by the ease of cleavage along (101). The shortest non-hydrogen bonded distances between molecules in adjacent sheets are: N_1–O, $2\cdot97$ Å; C–O, $3\cdot11$ Å; N_1–C, $3\cdot14$ Å; and N_1–N_1', $3\cdot18$ Å.

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Unit cell and space group of $NiK_2(SO_4)_2 . 6H_2O$.

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No X-ray data have been reported for $NiK_2(SO_4)_2 . 6H_2O$, one of the Tutton salts. Optical studies of Tutton and of Murmann and Rotter (Mellor, 1936) show the blue green prismatic crystals to be monoclinic. Data obtained in this laboratory confirm the symmetry and revise previously reported axial ratios.

The d values and relative intensities given in Table 1 were obtained from X-ray powder photographs using cobalt radiation. Lattice constants were determined by superposition of single crystal reflections of quartz on zero level Weissenberg photographs about the a and b axes. The monoclinic angle was taken from a zero level precession photograph. These data show

$$a = 6 \cdot 130 \pm 0 \cdot 002, \quad b = 12 \cdot 185 \pm 0 \cdot 004, \quad c = 8 \cdot 991 \pm 0 \cdot 002 \text{ Å},$$
$$\beta = 104° 59' \pm 3'.$$

The axial ratios found here are $0 \cdot 5031 : 1 : 0 \cdot 7379$ as compared to $0 \cdot 5020 : 1 : 0 \cdot 7379$ by Tutton and $0 \cdot 4965 : 1 : 0 \cdot 7374$ by Murmann and Rotter (Mellor, 1936). For $Z = 2$ the calculated density is $2 \cdot 237$ g.cm.$^{-3}$ which agrees with the observed density $2 \cdot 232$ g.cm.$^{-3}$ obtained by flotation methods. The single crystal photographs indicate the following conditions for non-extinction: $h0l$ present only for $l = 2n$ and $0k0$ present only for $k = 2n$. The space group therefore is $P2_1/c - C_{2h}^5$.

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Table 1. *Powder diffraction data for* $NiK_2(SO_4)_2 . 6H_2O$

d_o	I/I_0	hkl	d_o	I/I_0	hkl	d_o	I/I_0	hkl	d_o	I/I_0	hkl
6·08	20	020	3·29	20	$13\bar{1}$	2·433	5	$\begin{cases} 23\bar{1} \\ 14\bar{2} \end{cases}$	2·063	10	$\begin{cases} 222 \\ 24\bar{2} \end{cases}$
5·90	5	100	3·13	15	102	2·386	5	$\begin{cases} 221 \\ 230 \end{cases}$	2·039	15	024
5·31	20	110	3·04	30	$\begin{cases} 040 \\ 112 \end{cases}$	2·364	50	$13\bar{3}$	2·000	5	$30\bar{2}$
5·11	10	$11\bar{1}$							1·974	10	$\begin{cases} 31\bar{2} \\ 300 \end{cases}$
4·97	5	021	2·962	55	$\begin{cases} 21\bar{1} \\ 200 \end{cases}$	2·249	5	150			
4·35	20	002				2·231	5	$\begin{cases} 15\bar{1} \\ 10\bar{4} \end{cases}$	1·917	10	160
4·24	15	120	2·870	5	041				1·881	5	250
4·13	75	$\begin{cases} 111 \\ 12\bar{1} \end{cases}$	2·800	20	$20\bar{2}$	2·182	20	142	1·866	5	$\begin{cases} 15\bar{3} \\ 114 \end{cases}$
4·03	75	$10\bar{2}$	2·776	15	122	2·158	5	$\begin{cases} 212 \\ 24\bar{1} \end{cases}$	1·847	5	$31\bar{3}$
			2·727	15	$22\bar{1}$						
3·82	5	$11\bar{2}$	2·672	5	$14\bar{1}$	2·121	10	240	1·825	5	$\begin{cases} 33\bar{1} \\ 213 \end{cases}$
3·67	100	031	2·628	5	$12\bar{3}$	2·100	5	$\begin{cases} 14\bar{3} \\ 043 \end{cases}$	1·813	10	$16\bar{2}$
3·54	15	$\begin{cases} 121 \\ 022 \end{cases}$	2·546	5	$\begin{cases} 22\bar{2} \\ 211 \end{cases}$	2·090	5	$\begin{cases} 12\bar{4} \\ 15\bar{2} \end{cases}$	1·799	5	$\begin{cases} 14\bar{4} \\ 33\bar{2} \end{cases}$
3·35	10	130	2·485	10	$\begin{cases} 042 \\ 132 \end{cases}$						

Additional lines not listed.

The beryllides of Ti, V, Cr, Zr, Nb, Mo, Hf, and Ta.*

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A thorough X-ray diffraction study has been made of the

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* This work was performed under the auspices of the U.S. Atomic Energy Commission.

beryllides of Ti, V, Cr, Zr, Nb, Mo, Hf, and Ta. Table 1 shows the complete list of intermetallic compounds that are stable or metastable at room temperatures.

Cell dimensions heretofore not reported are given in