On pourrait également envisager l'assemblage des colonnes entre elles à l'aide d'un axe *An* parallèle à l'axe 2_1 qui est l'axe de la colonne; si nous n'envisageons qu'un réseau *P*, par exemple, le degré *n* de l'axe *An* doit être un multiple de celui de l'axe 2_1 et le groupe doit conserver ce dernier. Les groupes $P4_1$ et $P6_1$ répondent de ce critère.

(3) Le paramètre *b* qui caractérise la dimension de la colonne varie dans tous les sels étudiés entre 5,8 et 6,9 Å. Ce paramètre, de valeur constante, est lié au réseau de liaisons hydrogène, entre molécules de base et d'acide, organisé autour de l'axe 2_1.

Les molécules d'acide et de base se placent autour des atomes d'azote et d'oxygène du groupement $(\text{–COO})^-$ ainsi fixés, en respectant les distances moyennes de van der Waals.

Références

Brianso, M. C. (1976). *Acta Cryst.* B**32**, 3040–3045.

Brianso, M. C. (1978). *Acta Cryst.* B**34**, 778–781.

Brianso, M. C. & Surcouf, E. (1978). *Acta Cryst.* B**34**, 679–680.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Leclercq, M. & Jacques, J. (1975). *Bull. Soc. Chim. Fr.* pp. 2052–2056.

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1,2-Dihydro-3*H*-pyrazolo[3,4-*b*]pyridin-3-one

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Abstract. $C_6H_5N_3O$, $M_r = 135\cdot13$, monoclinic, $P2_1/c$, $a = 7\cdot976\,(2)$, $b = 6\cdot635\,(2)$, $c = 11\cdot362\,(3)$ Å, $\beta = 105\cdot04\,(2)^\circ$, $V = 567\cdot6$ Å^3, $Z = 4$, $D_m = 1\cdot52$ Mg m^{-3} (by flotation), $\mu(\text{Cu } K\alpha) = 0\cdot94$ mm^{-1}. The structure was solved by direct methods. The final R and R_w were 0·045 and 0·058 for 1003 independent reflections measured on the diffractometer. All non-hydrogen atoms of the molecule lie approximately in one least-squares plane. The π-electron delocalization in the pyrazolone ring is similar to that observed in peptide bonds. Two types of rather strong intermolecular hydrogen bonds between the carbonyl O and the two imino groups were found.

Introduction. The title compound was synthesized by cyclization of methyl α-chloronicotinate with hydrazine (Sehikawa, Nishie, Tono-oka, Tanaka & Kakimoto, 1973). The crystal structure investigations were undertaken to obtain structural information about the conformation of the compound. Similar compounds substituted at the C(6) position by methyl or phenyl groups have been synthesized (Balicki, Kaczmarek & Nantka-Namirski, 1976) in order to obtain new heterocyclic compounds possessing cytotoxic activity. The compound under investigation may serve as a good model molecule for the compounds mentioned above.

The crystals were obtained from an ethanol solution by slow evaporation. The crude unit-cell parameters and the space group were determined from rotational and Weissenberg photographs. Reflection intensities were collected on a CAD-4 automatic diffractometer (SLAF & BS, Jagiellonian University, Kraków) using the $\omega/2\theta$ scan technique up to $2\theta_{\max} = 120^\circ$. The back-

Table 1. *Atomic coordinates* ($\times 10^4$) *and* $B_{\text{eq.}}$ *values with standard deviations in parentheses*

	x	y	z	$B_{\text{eq.}}$ (Å^2)*
N(1)	8057 (2)	1805 (2)	3222 (1)	3·24 (7)
N(2)	8903 (2)	3096 (2)	4144 (1)	2·96 (7)
C(3)	8764 (2)	2504 (3)	5243 (2)	2·66 (7)
C(4)	7284 (2)	−801 (3)	5769 (2)	3·05 (8)
C(5)	6439 (3)	−2472 (3)	5190 (2)	3·48 (9)
C(6)	6140 (3)	−2677 (3)	3923 (2)	3·62 (9)
N(7)	6620 (2)	−1351 (2)	3191 (2)	3·55 (7)
C(7a)	7458 (2)	249 (3)	3781 (2)	2·74 (7)
C(8)	7818 (2)	623 (3)	5035 (2)	2·55 (7)
O	9361 (2)	3484 (2)	6221 (1)	3·36 (6)
Bonding H-atom coordinates ($\times 10^3$)				
H(N1)	850 (5)	171 (4)	238 (3)	
H(N2)	927 (4)	426 (4)	398 (2)	

* Calculated from anisotropic thermal parameters (deposited).

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ground was measured at each end of the scan for half the total scan time. 1003 independent reflections were measured with intensities above $2\sigma(I)$. The crystal structure was solved by direct methods using the *SHELX* program (Sheldrick, 1976). The positions of all the non-hydrogen atoms were obtained from the best E map. All H atoms were located on difference electron density maps, but only nitrogen hydrogens were included in the refinement process. The atomic positions for non-hydrogen atoms were refined by the anisotropic full-matrix least-squares procedure contained in the XRAY system (Stewart, Kundell & Baldwin, 1970). The final R factor was 0·045 and R_w with weights taken from counting statistics was 0·058. The atomic positional parameters are listed in Table 1.*

Discussion. Fig. 1 is an *ORTEP* (Johnson, 1965) diagram of the molecule showing the atom numbering. The bond lengths and angles are listed in Tables 2 and 3. The non-hydrogen atoms of the molecule lie approximately in one plane with a maximum deviation of about 0·03 Å. Planarity of the pyrazole ring was reported for 5*H*-pyrazolo[3,4-*d*]pyrimidine-4-thione (Gadret, Goursolle & Leger, 1974), 5-acetylamino-2,7-dimethylpyrazolo[1,5-*a*]pyrimidine (Ballard, Norris & Sheldrick, 1975) and 7-amino-2,5-dimethylpyrazolo[1,5-*a*]-pyrimidine hemihydrate (Mornon, Delettré & Bally, 1975), but in addition in all these cases a N(2)—C(3) double bond was observed. In the present case the conditions in the pyrazole ring are similar to those in cyclic polypeptides containing a *cis* peptide bond. The weighted average bond lengths for the amide bonds are C=O 1·24 and C—N 1·325 Å. The normal C—N bond length reported for cyclic peptides is about 1·34 Å (Karle, Gibson & Karle, 1970; Karle, 1974; Flippen & Karle, 1976). In the title compound the C(3)—N(2) bond distance is approximately the same as those in cyclic polypeptides but the C=O distance is longer than those reported previously. The planarity of the pyrazole ring suggests that a resonance form analogous to the amido–imino equilibrium characteristic for peptide bonding could be present. The N atoms in the pyrazole ring differ slightly from one another in the N—H bond lengths and geometry. Both H atoms belonging to the N(1) and N(2) atoms have been successfully located from the difference electron density maps with approximately the same density. The H(8) atom showing the shorter H—N distance [0·86 (2) Å] lies approximately in the least-squares plane of the molecule; the H(7) atom showing the longer [1·10 (2) Å] H—N distance deviates about 0·4 Å from this plane. This suggests that the hybridization of N(2) is approximately planar, whilst that of N(1) is more pyramidal.

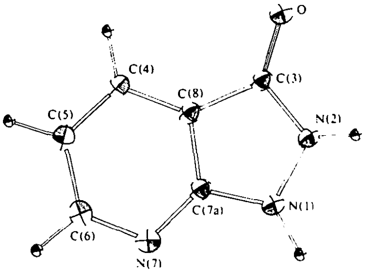

Fig. 1. *ORTEP* diagram (Johnson, 1965) of the molecule. Thermal ellipsoids are at the 40% probability level.

Table 2. *Interatomic distances* (Å) *with their standard deviations in parentheses*

N(1)—N(2)	1·385 (2)	C(4)—C(5)	1·374 (3)
N(1)—C(7a)	1·362 (2)	C(5)—C(6)	1·403 (3)
N(2)—C(3)	1·340 (2)	C(6)—N(7)	1·333 (3)
C(3)—O	1·269 (2)	C(7a)—C(8)	1·400 (2)
C(3)—C(8)	1·446 (2)	C(7a)—N(7)	1·338 (2)
C(4)—C(8)	1·398 (3)		

The O(1) atom is an acceptor in two fairly strong intermolecular hydrogen bonds (see Table 4) of nearly equal length (within two standard deviations) between donor and acceptor atoms but of different geometry. The existence of the shorter [1·65 (3) Å] distance from the acceptor to H(7) than that to H(8) [1·90 (2) Å] seems to be strictly related to the non-planarity of N(7). The projection of the crystal lattice along the a axis is shown in Fig. 2 with the hydrogen-bonding scheme. The overlapped molecules in Fig. 2 are related by the symmetry operation $2-x, -y, 1-z$.

Table 3. *Bond angles* (°) *with their standard deviations in parentheses*

N(2)—N(1)—C(7a)	106·1 (1)	C(6)—N(7)—C(7a)	113·4 (2)
N(1)—N(2)—C(3)	112·4 (2)	N(1)—C(7a)—N(7)	123·9 (2)
N(2)—C(3)—C(8)	105·5 (1)	N(1)—C(7a)—C(8)	109·6 (2)
N(2)—C(3)—O	124·3 (2)	N(7)—C(7a)—C(8)	126·5 (2)
O—C(3)—C(8)	130·3 (2)	C(4)—C(8)—C(7a)	118·2 (2)
C(5)—C(4)—C(8)	116·5 (2)	C(3)—C(8)—C(4)	135·5 (2)
C(4)—C(5)—C(6)	120·1 (2)	C(3)—C(8)—C(7a)	106·2 (2)
C(5)—C(6)—N(7)	125·1 (2)		

Table 4. *Hydrogen bonding in the crystal lattice*

A	D	D—H (Å)	$A\cdots$H (Å)	$D\cdots A$ (Å)	$\angle D$—H$\cdots A$ (°)
O(1)	N(1)($x, \frac{1}{2}-y, \frac{1}{2}+z$)	0·86 (2)	1·90 (2)	2·746 (2)	156 (2)
O(1)	N(2)($2-x, 1-y, 1-z$)	1·10 (2)	1·65 (3)	2·742 (2)	174 (2)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34460 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

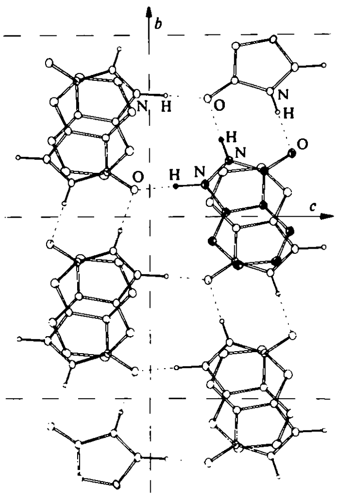

Fig. 2. *ORTEP* projection (Johnson, 1965) of the crystal structure along the *a* axis showing the hydrogen-bonding scheme. Non-bonding hydrogen atoms are omitted for clarity.

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References

Balicki, R., Kaczmarek, L. & Nantka-Namirski, P. (1976). *Acta Pol. Pharm.* **33**, 289–293.

Ballard, R. E., Norris, E. K. & Sheldrick, G. M. (1975). *Acta Cryst.* B**31**, 295–296.

Flippen, J. L. & Karle, I. L. (1976). *Biopolymers*, **15**, 1081–1092.

Gadret, M., Goursolle, M. & Leger, J. M. (1974). *Acta Cryst.* B**30**, 1598–1602.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Karle, I. L. (1974). *Biochemistry*, **13**, 2155–2162.

Karle, I. L., Gibson, J. W. & Karle, J. (1970). *J. Am. Chem. Soc.* **92**, 3755–3760.

Mornon, J. P., Delettré, J. & Bally, R. (1975). *Acta Cryst.* B**31**, 2119–2121.

Sehikawa, I., Nishie, J., Tono-oka, S., Tanaka, Y. & Kakimoto, S. (1973). *J. Heterocycl. Chem.* **10**, 931–932.

Sheldrick, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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Structure of 6-Bromo-1,2,3,4,4a,9a-hexahydro-4,9-dioxafluoren-2-one

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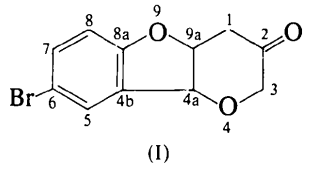
Abstract. $C_{11}H_9BrO_3$, $M_r = 269{\cdot}10$, monoclinic, $P2_1/a$, $a = 9{\cdot}145$ (1), $b = 10{\cdot}608$ (2), $c = 11{\cdot}104$ (2) Å, $\beta = 107{\cdot}08$ (1)°, $Z = 4$, $D_x = 1{\cdot}74$ Mg m^{-3}, μ(Cu $K\alpha$) = 5·89 mm^{-1}, $V = 1029{\cdot}2$ Å^3. The structure was solved by direct methods and refined by the least-squares procedure to a final R value of 0·076 (unit weights) using 1745 independent reflections. The chemical structure was fully confirmed. The pyran ring is in a boat ($B_{0,3}$) conformation.

Introduction. The title compound was obtained (Grynkiewicz, Krajewski, Urbańczyk-Lipkowska, Gluziński & Zamojski, 1979) as a side-product by Lewis-acid-catalyzed substitution of 6-benzyloxy-2H-pyran-3(6H)-one by p-bromophenol. Its chemical structure was not clear initially and therefore X-ray structural investigations were performed in order to verify the conclusions drawn from the spectrochemical data.



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