0·240 Å.; 12° intervals along c, every 0·222 Å; and 12° intervals along [011], every 0·328 Å. The positions of the contour lines were obtained from the summation totals by graphical interpolation.

A final Fourier section in (011) was constructed, based on the calculated structure factors in Table 2, for comparison with Fig. 5. The two maps were sufficiently similar to exclude any new information being yielded about the position of the atomic centers. The greatest difference found between the two sections at any point was 0·5 e.Å^{-3}, and the principal effect was to raise the level of the background from a small negative to a small positive electron density. The peak positions did not show any appreciable alteration.

References

Abrahams, S. C., Collin, R. L., Lipscomb, W. N. & Reed, T. B. (1950). *Rev. Sci. Instrum.* **21**, 396.

Andrew, E. R. (1950). *J. Chem. Phys.* **18**, 607.

Bruni, G. & Natta, G. (1929). *Rec. Trav. chim. Pays-Bas*, **48**, 860.

Bruni, G. & Natta, G. (1930). *R.C. Accad. Lincei* (6), **11**, 929.

Cox, E. G. (1932). *Proc. Roy. Soc.* A, **135**, 491.

Cox, E. G., Gillot, R. J. J. H. & Jeffrey, G. A. (1949). *Acta Cryst.* **2**, 356.

Evans, M. G. & Heer, J. de (1949). *Acta Cryst.* **2**, 363.

Harker, D. (1948). *Amer. Min.* **33**, 674.

Internationale Tabellen (1935). Berlin: Borntraeger.

Longuet-Higgins, H. C. (1948). *Trans. Faraday Soc.* **45**, 173.

Lumbroso, H. (1949). *C.R. Acad. Sci. Paris*, **228**, 77.

Pauling, L. (1930). *Phys. Rev.* **36**, 430.

Robertson, J. M. (1948). *J. Sci. Instrum.* **25**, 28.

Schomaker, V. & Pauling, L. (1939). *J. Amer. Chem. Soc.* **61**, 1769.

Ubbelohde, A. R. (1950). *Quarterly Reviews*, **4**, 356.

Waddington, G., Knowlton, J. W., Scott, D. W., Oliver, G. D., Todd, S. S., Hubbard, W. N., Smith, J. C. & Huffman, H. M. (1949). *J. Amer. Chem. Soc.* **71**, 797.

Wilson, A. J. C. (1942). *Nature, Lond.*, **150**, 152.

Acta Cryst. (1952). **5**, 99

The Crystal Structure of 2-Metanilamido-5-Br-Pyrimidine*

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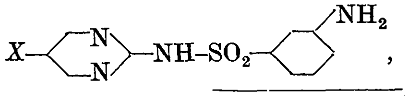
(*Received* 21 *April* 1949 *and in revised form* 13 *March* 1951)

The crystal structure of 2-metanilamido-5-Br-pyrimidine, $C_{10}H_9BrN_4O_2S$, and its isomorphous iodine analog, has been determined by two-dimensional Fourier methods. These compounds are active anti-malarials. The crystals are monoclinic space group $P2_1/n$. A 'subtraction Fourier' method is described which was helpful in obtaining the signs of weak reflections. The method may prove useful in cases where a heavy scatterer, used to determine the phases of the stronger reflections, obscures the detail of the lighter atoms. The analysis is based mainly on one well-resolved projection, and on a combination of the Pauling covalent radii with the essential structural features disclosed by the second, heavily overlapped, projection of the molecule. The configuration of the –NH–SO$_2$– linkage between aromatic rings is given for the first time. Weak hydrogen-bonding between NH$_2$ and oxygen atoms of SO$_2$, of length 3·15 Å, is indicated, with one hydrogen of the NH$_2$ group of one molecule directed to one of the oxygens of an adjacent molecule.

Interest has recently been shown in the structure of pyrimidines (Clews & Cochran, 1948, 1949; Pitt, 1948). These analyses have demonstrated that the pyrimidine ring, while not a regular hexagon, is probably planar. Evidence is given that the C–N bonds are about 0·03 kX. shorter than the C–C bonds. The present analysis, of the compound (1),



, X = Br or I, (1)

is not precise enough to contribute to the knowledge of the details of the pyrimidine ring. However, some detail was obtained for the frequently encountered –NH–SO$_2$– linkage between the aromatic rings.

Compound (1), together with a large number of related substances, was described in a paper on anti-malarials from the Stamford Research Laboratories of the American Cyanamid Company (English, Clark, Shepherd, Marson, Krapcho & Roblin, 1946). The chlorine, bromine, and iodine analogues of compound (1) were given to us by the authors; these compounds are active anti-malarials. It was felt that there was a possibility of isomorphism in this series, which, if substantiated, could contribute to the solution of the

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structure (Robertson & Woodward, 1940; Bunn, 1945, chap. 10). The bromine and iodine compounds were indeed found to be isomorphs.

Small single crystals were obtained by slow cooling of hot glacial acetic acid solutions in micro-tubes. The crystals are biaxial negative; α is the acute bisectrix and its direction parallels the needle, or c, axis; $2V$ is 65° for the bromine compound in glycerine. The crystals are monoclinic.

Weissenberg diagrams were obtained about the c and b axes with filtered Cu $K\alpha$ radiation. The intensities were estimated visually with the aid of an intensity scale and the multiple-film technique (Robertson, 1943). The scale consisted of small uniform spots made with crystal-monochromatized Cu $K\alpha$ radiation attenuated by nickel foils placed between the monochromator and the film strips. The beam was directed through a small hole in a lead sheet to the package of film strips which were interleaved with black paper, thus duplicating the conditions for the multiple-film Weissenbergs. A series of timed exposures was arranged to give a suitable intensity scale on the fourth film strip. The strips further provided a means for determining the absorption factor, found to be 4, to be used between successive films.

Systematic extinctions for the axes chosen gave $P2_1/n$ as the space group. The lattice constants are given in Table 1. There are four molecules per unit cell (4·04 calc.). No measurements were made on the chlorine analogue after its crystal structure was observed to be different from that of the other two.

Table 1. *Axes of reference*

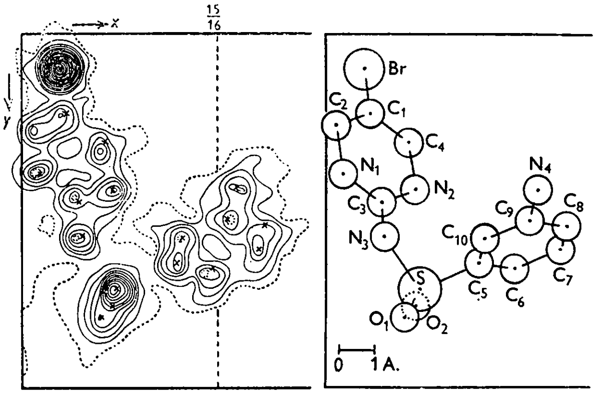
	a (kX.)	b (kX.)	c (kX.)	β (°)
Iodine compound	22·0	9·70	5·66	92·5
Bromine compound	21·9	9·53	5·63	92·5

The zero-layer Weissenberg diagram with rotation about the needle axis was obtained with an exposure of about 1000 mA. hr.; about 160 $hk0$ reflections were recorded. It seemed evident that this zone would suffer least from overlapping of atoms in projection, so that most care was given to the $hk0$ data and its analysis. Lorentz and polarization-factor corrections were applied to the intensities to give the F^2 values, absorption errors having been considered serious only with the data obtained about the b axis, which lay across the needle. The crystals used were about 0·5 mm. long and 0·05 mm. thick, the cross-sections roughly approximating a hexagon.

In outline, the analysis consisted of two-dimensional F^2 and F series computed for the $hk0$ and $h0l$ projections. The Patterson projections were readily analyzed for the halogen parameters, and later for those of the sulfur atoms; the isomorphism was of assistance in this process. Successive trial Fourier projections of electron density, chiefly on the c face, outlined the main features of the molecule. Fairly good intensity checks were obtained with the refined halogen and sulfur parameters, but the positions of the lighter atoms remained uncertain. A 'subtraction Fourier' technique was devised which made use of a large number of weak reflections and fortunately disclosed the positions of most of the light atoms. The parameters given in Table 3 are based on the following: (1) the adequately resolved $hk0$ projection of electron density (Fig. 1 (a)); (2) the complementary, although less well resolved, $h0l$ projection (Fig. 3); (3) the compatibility with packing requirements; and (4) the quality of the intensity checks (Table 2)*.

Table 3. *Atomic parameters*

	x	y	z
Br	0·048	0·100	0·275
C_1	0·055	0·220	0·025
C_2	0·013	0·255	0·875
C_3	0·072	0·483	0·838
C_4	0·105	0·303	0·076
N_1	0·023	0·400	0·773
N_2	0·115	0·447	0·989
N_3	0·078	0·573	0·640
S	0·122	0·723	0·692
O_1	0·102	0·800	0·473
O_2	0·115	0·768	0·945
C_5	0·197	0·648	0·667
C_6	0·245	0·665	0·827
C_7	0·300	0·610	0·765
C_8	0·308	0·540	0·528
C_9	0·262	0·525	0·368
C_{10}	0·205	0·578	0·433
N_4	0·272	0·445	0·153



(a) (b)

Fig. 1. (a) Fourier plot of one molecule, $hk0$ projection. Each contour represents an increment of 1 e.Å^{-2}, except around the Br and S atoms where the value is doubled. The 1-electron line is dotted. Dotted contours at peak regions represent about one-half electron.

(b) Plan of one molecule corresponding to the Fourier projection. The spheres are of arbitrary sizes, centered at positions marked with crosses in (a). Relative heights are indicated by the way the 'atoms' are connected.

The overall intensity agreement, as represented by the correlation coefficient $\Sigma\,|\,F_o - F_c\,|\div\Sigma F_o$, is 0·25

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* Table 2, which lists observed and computed F values for 240 $hk0$ reflections and 90 $h0l$ reflections, is not reproduced but has been deposited with the American Documentation Institute, 1719 N Street, North-west, Washington 6, D.C., U.S.A. under reference 3270. Microfilms or photocopies can be obtained from the Institute, price $1.00.

for the *hk*0 reflections and 0·22 for the *h*0*l* reflections. As only Beevers–Lipson strips, giving amplitudes of Fourier terms for each $\frac{1}{60}$ of a unit cell edge, and ordinary computers were used, no attempt was made to refine the *b*-face projection.

Relative intensities were used for the two-dimensional Patterson series. All the atoms are in four-fold general positions. Analysis of the Patterson projections on the *b* and *c* faces resulted in two possible positions for the halogen atom. Intensity calculations eliminated structures based on one of these positions; the parameters given by the other were shown finally to have been correct within 0·005 of the cell edges. The Patterson projections for the bromine and iodine isomorphs left little doubt, when compared, as to which peaks were due to halogen–halogen interactions, even though relative intensities had been used. The isomorphism was of further aid in identifying the halogen–sulfur interactions.

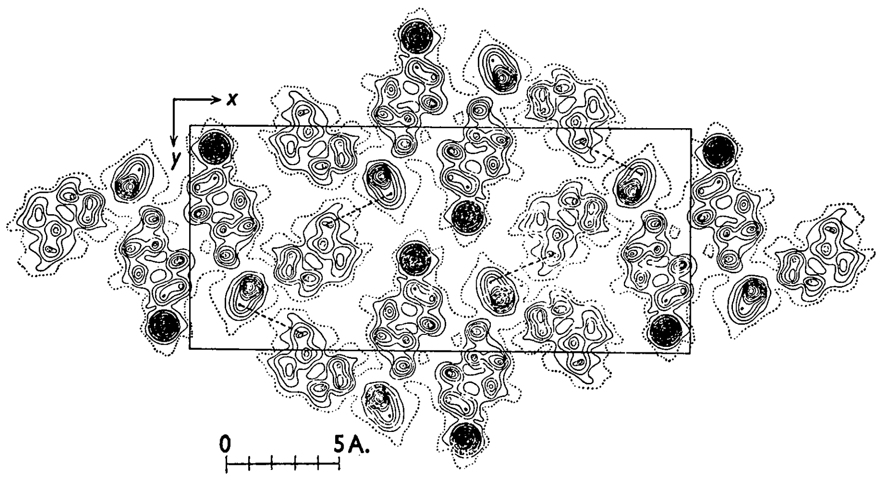

Fig. 2. The Fourier map of the contents of a unit cell plus four adjacent molecules in the *hk*0 projection. Contours as in Fig. 1(*a*). Broken lines represent hydrogen bonds.

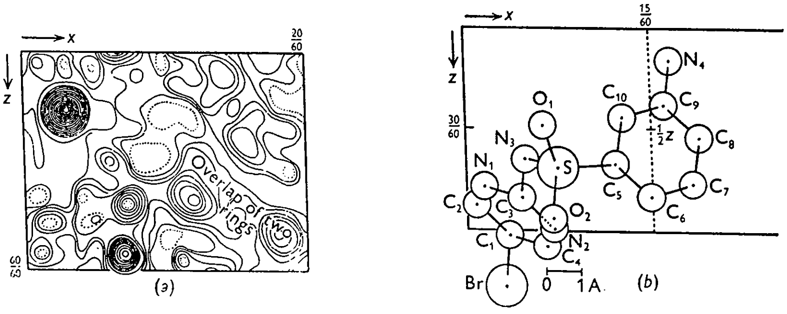

Fig. 3. (*a*) Fourier plot of part of unit-cell contents. Contours as in Fig. 1(*a*). (*b*) Plan of one molecule in the *h*0*l* projection.

The first *F*-series trials were made for the *hk*0 zone. Phases were computed for the stronger *hk*0 reflections, using only the halogen contribution to the structure factors. While this permitted the assignment of signs with reasonable certainty to only one-third of the 160 observed *hk*0 points, the resulting *F* series permitted two interpretations to be made of the molecular configuration and particularly of the position of the sulfur atom. Intensity calculations again pointed to the correct choice, and use of the Patterson diagrams helped to define the sulfur parameters. Extensive intensity calculations with the halogen and sulfur contributions showed sufficiently good agreement with the observed data to provide a scaling factor for placing the observed *F* values on an approximately absolute scale. The temperature factor could also be estimated at $3{\cdot}5$ Å^2. At this stage, about two-thirds of the *hk*0 amplitudes could be assigned phases with reasonable assurance. Several more trial Fourier series indicated that the process of refinement would be very tedious, if at all possible, without going to three-dimensional methods; the *h*0*l* projection was even less clear.

It seemed interesting to see what sort of projection would result if the contributions of the 'obscuring' halogen atom were subtracted from the structure amplitudes. It was soon observed that the bromine contribution could be removed from a large number of very weak reflections, including many within range of the film and the radiation which had not registered on the film at all, and leave a residue, consisting of the contributions of the lighter atoms, to which a sign could confidently be given. Thus,

$$F'_{hk0}=F_{hk0}-f_{hk0},$$

where F' is the sum of the contributions of the lighter atoms, f is the temperature-corrected bromine contribution, and F is the observed and corrected structure factor. F'_{hk0} terms were computed in this manner for a large number of $hk0$ reflections, including those of zero intensity within range. The 'subtraction Fourier' series was computed with those residues to which signs could be assigned. The resulting plot disclosed reasonable positions for most of the light atoms. All these new positions contributed to a large number of improved intensity checks, and the signs so obtained, when used in the next normal Fourier trial, gave all the necessary additional detail. The subsequent stage of refinement was the final one, with the signs determined for all but one or two of the 160 observed $hk0$ reflections. While the applicability of similar subtraction methods is obviously limited, their use may save trial and error in some cases.

The parameters of Tables 3 and 4 are based on the assumption of regular plane hexagons of sides 1·39 Å for the two rings. Projection of a model was used to obtain the parameters, in combination with intensity calculations, so that precise bond lengths in the rings cannot be claimed for this analysis. Pauling's (1945) covalent radii were assumed to apply, and no evidence to the contrary appeared. Pyrimidine structures previously published (Clews & Cochran, 1948, 1949; Pitt, 1948) claim an irregular hexagon for the pyrimidine ring. The only indication of this in the present analysis might be the contours in the region of the carbon atom C_4; however, the intensity calculations were not sufficiently sensitive to provide adequate evidence concerning this question.

Table 4. *Bond lengths, angles, and other distances*

Distances within the rings are not included as the rings were taken to be regular hexagons of approximately 1·39 Å per side. The resolution was insufficient to arrive at independent measurements of these intra-ring bonds.

	Measured (Å)	Calculated from Pauling's radii (Å)
Br–C_1	1·90 ± 0·04	1·90
C_3–N_3	1·42 ± 0·06	1·45
N_3–S	1·75 ± 0·04	1·74
S–O_1	1·50 ± 0·04	1·52
S–O_2	1·50*	1·52
S–C_5	1·80 ± 0·04	1·80
N_3–N_1†	2·18 ± 0·06	—
N_3–N_2†	2·44 ± 0·06	—

Oxygen of one molecule to N_4 of other molecules‡:
3·15, ± 0·04 Å:

Pyrimidine ring –C_3–N_3	145° ± 5°
C_3–N_3–S	113° ± 3°
N_3–S–C_5	100° ± 3°
O_1–S–O_2	132° ± 5°
Plane of SO_2 group with plane of N_3–S–C_5	80° ± 5°
Plane of C_3–N_3–S with plane of N_3–S–C_5	50° ± 5°

(These and other angles in the NH–SO_2 linkage appear in Fig. 4.)

* Length assumed; resolution poor.
† These atoms are not bonded.
‡ Hydrogen bonds.

The configuration of the $>$C–NH–SO_2–C$<$ linkages is, however, independently derivable from this analysis (Fig. 4). The projection on the b face confirms what is indicated by the c-face projection regarding the approximate parallelism of the NH–S–C bonds to that face. Also of interest is the possibility of hydrogen bonding molecules. The amino-nitrogen atom (N_4) of one molecule may be linked through a weak hydrogen bond with the oxygen of an adjacent molecule. The distance is 3·15 Å between N_4 and O_1, but the closest approach of an N_4 to an O_2 is 3·76 Å. If the 3·15 Å separation means hydrogen bonding, we can represent the situation by the following:

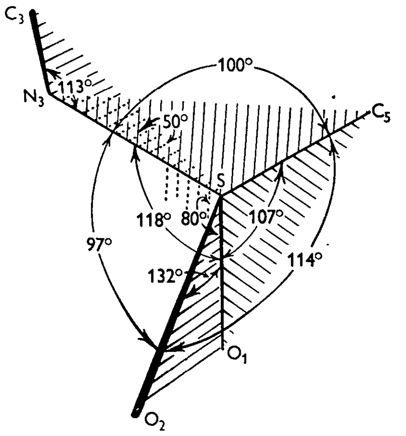

Fig. 4. Configuration of the –NH–SO_2– linkage. This diagram is not drawn to scale, but is intended to give some picture of the angles among the bonds and planes of bonds, as tabulated in Table 4. The view is roughly that of Fig. 1.

Designate the molecule whose atoms are at general positions (x, y, z) as molecule no. 1. Its atoms will be referred to by the superscript '1'. Then, the other three molecules arising from it by the symmetry operations (the 2_1 screw and the n-glide) may be referred to as molecules nos. 2, 3 and 4, with no. 2 created from no. 1 by the glide, no. 3 from no. 1 by the screw axis, and no. 4 from no. 3 by the glide. Using the superscripts to describe the molecule to which each atom belongs, we find that the hydrogen bonding occurs between

N_4^1 and O_1^3,
N_4^2 and O_1^4,
N_4^3 and O_1^1,
and N_4^4 and O_1^2.

Thus the hydrogen bonding makes two separate networks of molecules, the molecules within each network being bonded, but with no bonding between networks (Fig. 2).

Regarding the compatibility of this hydrogen bond with others, the 3·15 Å distance is in the range of hydrogen bonds involving nitrogen. Layers of glycine molecules (Albrecht & Corey, 1938) are hydrogen bonded across a distance of 3·0 Å. Robertson (1940) refers to the glycine case in a general discussion wherein he makes note of the longer hydrogen bond to be expected between nitrogen and oxygen, as compared with oxygen to oxygen, owing to the lesser electronegativity of nitrogen. A recent analysis of the crystal structure of *p*-nitroaniline (Abrahams & Robertson, 1948) includes a hydrogen bond of about 3·1 Å between nitrogens, linking an amino-nitrogen with a nitro-nitrogen atom.

Bond lengths and other spacings are given in Table 4 and Fig. 4.

The interest and helpfulness of Dr D. Crowfoot and Dr J. Gillis are gratefully acknowledged. We are indebted to Dr J. P. English, of the Stamford Research Laboratories, for the compounds and for helpful discussions.

References

ABRAHAMS, S. C. & ROBERTSON, J. M. (1948). *Acta Cryst.* **1**, 252.
ALBRECHT, G. & COREY, R. B. (1938). *J. Amer. Chem. Soc.* **60**, 1598.
BUNN, C. W. (1945). *Chemical Crystallography.* Oxford: Clarendon Press.
CLEWS, C. J. B. & COCHRAN, W. (1948). *Acta Cryst.* **1**, 4.
CLEWS, C. J. B. & COCHRAN, W. (1949). *Acta Cryst.* **2**, 46.
ENGLISH, J. P., CLARK, J. H., SHEPHERD, R. G., MARSON, H. W., KRAPCHO, J. & ROBLIN, R. O. Jr. (1946). *J. Amer. Chem. Soc.* **68**, 1039.
PAULING, L. (1945). *The Nature of the Chemical Bond.* Ithaca: Cornell University Press.
PITT, G. J. (1948). *Acta Cryst.* **1**, 168.
ROBERTSON, J. M. & WOODWARD, I. (1940). *J. Chem. Soc.* p. 36.
ROBERTSON, J. M. (1943). *J. Sci. Instrum.* **20**, 175.
ROBERTSON, J. M. (1940). *Trans. Faraday Soc.* **36**, 913.

Acta Cryst. (1952). **5**, 103

Structural Interpretation of the Diaspore–Corundum and Boehmite–γ-Al_2O_3 Transitions*

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(*Received* 24 *July* 1950 *and in revised form* 26 *March* 1951)

Transitions from hydrated to anhydrous compounds are treated as transformations *in situ*, with special attention to effects of the limited opportunity for atomic rearrangement which accompanies such transformations. The diaspore–corundum group is characterized by oxygen atoms in hexagonal close-packing as distinct from the boehmite–γ-Al_2O_2 group which is based on oxygens in cubic close-packing. Detailed microscopic and X-ray data are cited to show that corundum preserves the structural orientation of the diaspore crystals from which it is produced by dehydration.

The new group of γ-Al_2O_2-type structures is discussed, and it is suggested that the supposition of 'order–disorder' phenomena in the γ-Al_2O_3 structure provides a reasonable explanation for the existence of the new forms.

Introduction

Aluminum oxide exists in two forms, γ-Al_2O_3 and corundum, whose properties contrast to a high degree. The same contrast is carried over to the two forms of the monohydrate of aluminum oxide, boehmite and diaspore, with boehmite resembling γ-Al_2O_3 and diaspore resembling corundum. Thermal dehydration of either of the trihydrates, gibbsite and bayerite, or of hydrous alumina gel yields only boehmite followed by γ-Al_2O_3, while diaspore dehydrates to corundum and is formed only under hydrothermal conditions. These facts led Haber and others to designate the group composed of gibbsite, bayerite, boehmite and γ-Al_2O_3 as the γ series and the group diaspore and corundum as the α series. In this paper it is shown that there are structural relationships between the compounds in each series which account for the similarities in their properties and the reluctance of members of one series to transform to the other. The structural basis is also employed to explain the recent finding of several additional forms of anhydrous aluminum oxide which are of great practical importance as activated aluminas.

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* Taken in part from a thesis submitted by the author to the Pennsylvania State College in partial fulfillment of the requirements for the Ph.D. degree, September 1949.

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