

Table 6. *Hydrogen-bond distances (Å) and angles (°)*

$X-H \cdots Y$	$X \cdots Y$	$X-H$	$H \cdots Y$	$X-H \cdots Y$	Symmetry operation on Y
N(3)-H(3)···O(6)	2.598 (6)	0.82 (5)	1.98 (5)	131 (5)	x, y, z
N(8)-H···O(14)	2.921 (6)	0.88 (5)	2.13 (4)	150 (4)	$1 - x, -y, 2 - z$
N(10') ⁺ -H···O(9)	2.797 (6)	0.98 (5)	1.87 (5)	158 (5)	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z + 1$
O(13)-H···O(10)	2.461 (5)	0.71 (8)	1.81 (8)	152 (8)	$x, 1 + y, z$

References

- BLACK, J. W., DUNCAN, W. A. M., DURANT, C. J., GANELLIN, C. R. & PARSONS, E. M. (1972). *Nature (London)*, **236**, 385-390.
- BRADSHAW, J., BRITAIN, R. T., CLITHEROW, J. W., DALY, M. J., JACK, D., PRICE, B. J. & STABLES, R. (1979). *Br. J. Pharmacol.* **66**, 464P (Abstract).
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891-1898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321-324.
- LANGMAN, M. J. S., HENRY, D. A., BELL, G. D., BURNHAM, W. R. & OGILVY, A. (1980). *Br. Med. J.* **281**, 473-474.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- PEDEN, N. R., SAUNDERS, J. H. B. & WORMSLEY, K. G. (1979). *Lancet*, pp. 690-692.
- PROUS, J. R. (1979). Editor. *Annual Drug Data Report*, Vol. IV, No. 9, pp. 663-666. Provenza, Barcelona: J. R. Prous.
- SIMON, B. & KATHER, H. (1979). *Disch. Med. Wochenschr.* **104**, 1676-1678.
- STEWART, J. M., MACHIN, P. A., DICKINSON, C., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.
- THOMAS, J. O. & RENNE, N. (1975). *Acta Cryst.* **B31**, 2161-2163.
- TOSO, R., DECORTE, E., ZONNO, F. & ŠUNJIĆ, V. (1981). *Acta Pharm. Jugosl.* In the press.
- WOODINGS, E. P., DIXON, G. T., HARRISON, C., CAREY, P. & RICHARDS, D. A. (1980). *Gut*, **21**, 187-191.

Acta Cryst. (1982). **B38**, 1840-1843

Structure of 2,4,6-Triaminopyrimidine*

BY CARL H. SCHWALBE AND GRAHEME J. B. WILLIAMS†

Department of Pharmacy, The University of Aston in Birmingham, Gosta Green, Birmingham B4 7ET, England, and Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, USA

(Received 14 July 1981; accepted 28 January 1982)

Abstract. $C_4H_7N_5$, $M_r = 125.1$, monoclinic, $P2_1/n$, $a = 10.348$ (3), $b = 9.551$ (2), $c = 12.464$ (9) Å, $\beta = 112.27$ (4)°, $U = 1140.0$ Å³, $Z = 8$, $D_c = 1.46$, $D_m = 1.45$ g cm⁻³, $\mu(\text{Cu } K\alpha) = 8.75$ cm⁻¹, final $R = 0.107$ for 995 independent reflections. Transparent crystals grow from aqueous ethanol/acetone solution as twinned needles with the c repeat parallel to the needle axis. The two independent molecules are nearly planar but deviate up to 0.03 (1) Å from the expected local

C_{2v} symmetry. Molecules are joined into ribbons by N-H···N bonds linking 4- and 6-amino groups to ring nitrogen atoms. Two ribbons associate by π - π interactions between equivalent molecules to form an infinite antiparallel double ribbon; the 2-amino substituents of different molecules approach each other in a manner which suggests they both donate and accept hydrogen bonds.

Introduction. Antifolate drugs are found to associate in the crystalline state *via* dimeric N-H···N interactions with exocyclic amino groups as proton donors and ring nitrogen atoms as proton acceptors. An additional mode of N-H···N hydrogen bonding between tetra-

* Research carried out at Brookhaven National Laboratory under contract with the US Department of Energy and supported by its Office of Basic Energy Sciences.

† Present address: Enraf-Nonius, 390 Central Avenue, Bohemia, NY 11716, USA.

hedrally distorted groups in the antifolate drug 2,4,6-triamino-5-chloroquinazoline (TCQ), each acting both as a proton donor and as a proton acceptor, was found by Rogan & Williams (1980). This tetrahedral distortion is thought to imply partial sp^3 rehybridization which may be important in rationalizing the enhanced binding of dihydrofolate reductase (DHFR) inhibitors to the enzyme (Hunt, Schwalbe, Bird & Mallinson, 1980). We report here the structure of 2,4,6-triaminopyrimidine which is a modestly effective DHFR inhibitor (Baker & Santi, 1965). Like TCQ, this molecule also has three amino groups and two ring nitrogen atoms. Furthermore, all of its nitrogen atoms can be superimposed on those of the important diaminopteridine DHFR inhibitors such as amethopterin.

Experimental. A sample of the title compound (purchased from Sigma Chemical Company) in a mixture of aqueous ethanol and acetone yielded laths and fine needles upon slow evaporation of solvent. The laths consisted of laminated needles, as evidenced by their striated appearance, incomplete extinction under the polarizing microscope, and the stepped ends of some of them. A lath of dimensions $0.84 \times 0.09 \times 0.04$ mm possessing unusually regular and shiny faces was selected for crystal-structure analysis.

A large triclinic unit cell with $Z = 24$ was originally deduced by the auto-indexing routine of the Enraf-Nonius CAD-4 system. Previously taken precession photographs appeared to corroborate this information but upon close inspection it was found that the reflection set could be split into two monoclinic subsets. The c axis parallels the long axis of the lath. The cell has an approximately square cross section when viewed parallel to c , $b = 9.551(2) \text{ \AA}$ and $a \sin \beta = 9.576(3) \text{ \AA}$. In reciprocal space this relationship appears even more exact with $b^* = 0.1044 \text{ \AA}^{-1}$ and $a^* = 0.1047 \text{ \AA}^{-1}$. This condition favors twinning and we have shown from the two orientation matrices that the specimen crystal was composed of two components which were related by reflection through the plane (110). By indexing the reflections of the minor twin component in the axial system of the major we inferred that a reflection with indices hkl in the satellite system has apparent indices $-k - l/3, h - l/3, l$ in the axial system of the main crystal. The reflections with $l = 3n$ from the major component are therefore contaminated by the minor component.

Intensity data were collected on a CAD-4 diffractometer with graphite-monochromated $\text{Cu } K\alpha$ radiation, yielding 4355 reflections with $2\theta < 125^\circ$. The crystal was considered to be an infinitely long needle and rotated around ψ to the position of minimum absorption for each reflection. The 1945 unique data had a Wilson (1942) scale factor of 1.80 and were successfully used in structure determination by *SHELX76* (Sheldrick, 1976). Only the 1186 re-

Table 1. Atomic coordinates and equivalent isotropic vibration terms for the non-hydrogen atoms

Coordinates have been multiplied by 10^4 , U_{iso} by 10^3 .

	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$
N(1)	3767 (6)	3418 (7)	3492 (5)	30 (2)
C(2)	4218 (7)	3046 (8)	4602 (6)	23 (3)
N(2)	5054 (8)	1892 (9)	4908 (6)	41 (3)
N(3)	3924 (6)	3642 (7)	5474 (5)	30 (3)
C(4)	3072 (8)	4754 (9)	5138 (6)	32 (3)
N(4)	2733 (8)	5353 (9)	5999 (5)	39 (3)
C(5)	2516 (8)	5263 (9)	4005 (7)	39 (3)
C(6)	2917 (8)	4534 (9)	3222 (6)	33 (3)
N(6)	2420 (8)	4938 (9)	2082 (6)	47 (3)
N(1')	3416 (7)	3752 (8)	-1639 (5)	32 (3)
C(2')	3040 (7)	4192 (9)	-763 (6)	27 (3)
N(2')	1855 (7)	5014 (8)	-1097 (6)	36 (3)
N(3')	3620 (7)	3898 (7)	369 (5)	32 (3)
C(4')	4746 (7)	3076 (8)	664 (6)	28 (3)
N(4')	5363 (8)	2751 (8)	1823 (6)	38 (3)
C(5')	5260 (8)	2534 (9)	-122 (6)	38 (3)
C(6')	4561 (8)	2908 (9)	-1277 (6)	31 (3)
N(6')	4942 (8)	2428 (9)	-2149 (7)	42 (3)

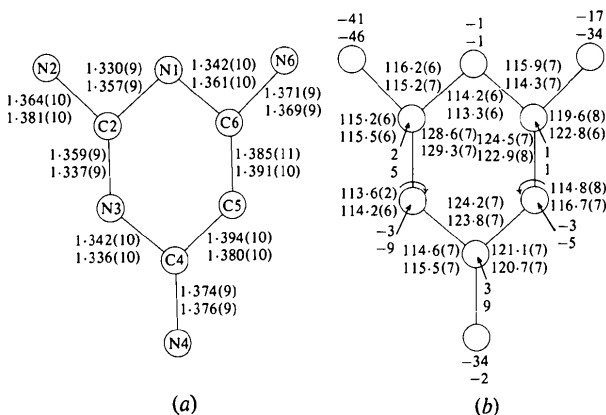


Fig. 1. (a) Nomenclature for the non-hydrogen atoms and bond distances (\AA) in the two crystallographically independent molecules. Distances in the molecule comprised of the primed atoms are given below their counterparts. (b) Interbond angles ($^\circ$) for the non-hydrogen atoms and deviations ($\text{\AA} \times 10^3$) from the mean plane defined by the six atoms of the pyrimidine ring. Angles and displacements for the primed atoms are given below their counterparts. The average standard deviation in the displacement of an atom from the plane is 0.003 \AA .

flections with $l \neq 3n$ were used further, their considerably higher Wilson scale factor of 2.15 reflecting the lack of contamination from the satellite crystal. Least-squares refinements utilized the 995 data with $F > 3\sigma$ after Gaussian absorption correction (Busing & Levy, 1957) (range of transmittances from 0.871 to 0.965). All hydrogen atoms were located in difference Fourier syntheses except for one from each 2-amino group, which was therefore placed in an idealized position. Hydrogen atoms were assigned isotropic U terms of 0.1 \AA^2 . With a weighting scheme of $w =$

$k[\sigma^2(F_o) + gF_o^2]^{-1}$ the least-squares refinement converged with $k = 4.7275$ and $g = 0.0004$ at $R = 0.104$, $R_w = [\sum w\Delta^2 / \sum wF_o^2]^{1/2} = 0.098$. Final atomic coordinates are given in Table 1, atomic nomenclature, bond lengths, bond angles and departures from planarity are given in Fig. 1.*

Discussion. By inspection of the atomic coordinate table it can be seen that the two crystallographically independent molecules are related by the pseudo symmetry element, $x', y', z' \approx y, x, z - 0.4$. This corresponds to a pseudo c -glide plane normal to the ab face diagonal. That this operation is non-crystallographic is clear from the 0.4 translation but it is interesting to note that this pseudo glide operation is expressed in the mirror twin law for this material which was independently derived.

In the absence of crystal packing forces one would expect C_{2v} molecular symmetry for 2,4,6-triaminopyrimidine. In the crystal differences up to 0.03 \AA (2.1σ) and 2° (1.8σ) between these chemically equivalent bond distances and angles within the same molecule are observed, and of a similar order between the two independent molecules. The planarity of the molecules is very little disturbed, no ring atom deviating by as much as 0.01 \AA from its least-squares plane, Fig. 1(b). Even the exocyclic amino nitrogen atoms deviate by 0.046 (3) \AA or less.

Both base-stacking and base-pairing interactions are exemplified in this structure. The two crystallographically independent molecules are hydrogen bonded into infinite $ABAB \dots$ chains in the c direction as illustrated in Fig. 2. An intra-chain hydrogen-bond-like interaction involving the 2-amino groups of two non-crystallographically related molecules is also indicated. The intra-chain distances are: $N(4')\text{---}H \cdots N(1) = 3.169$ (7) \AA and $N(6)\text{---}H \cdots N(3') = 3.017$ (8) \AA for one linkage and $N(6')\text{---}H \cdots N(3) = 2.984$ (7) \AA and $N(4)\text{---}H \cdots N(1') = 3.151$ (8) \AA for the other. The intra-chain interaction involving pendant $N(2)$ and $N(2')$ groups has $N(2') \cdots H(21)$ of 2.26 (5) \AA and $H(21) \cdots N(2')\text{---}C(2')$ of 94 (1) $^\circ$, thus indicating that the H atom approaches in the direction of the N atom's lone pair and is within van der Waals distance. A similar interaction involving $N(2)$ as H-bond acceptor from $H(21')$ is too long to be considered a hydrogen bond [2.56 (2) \AA] but otherwise has the same features as the $H(21) \cdots N(2')$ linkage. Contacts similar to these have been noted by Kvick & Noordik (1977) and Rogan & Williams (1980).

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36654 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

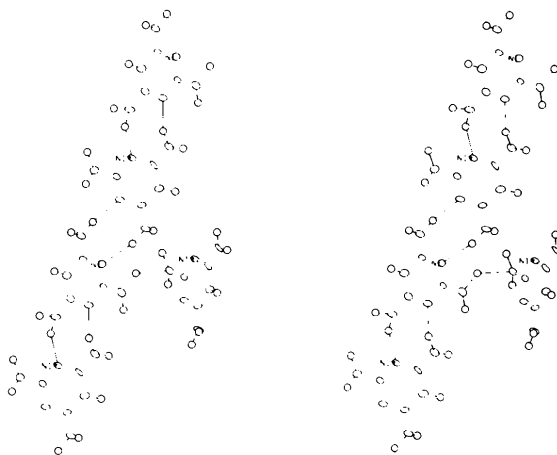


Fig. 2. An ORTEP (Johnson, 1976) illustration showing a segment of the hydrogen-bonded chain and the inner-chain hydrogen-bond-like linkage.

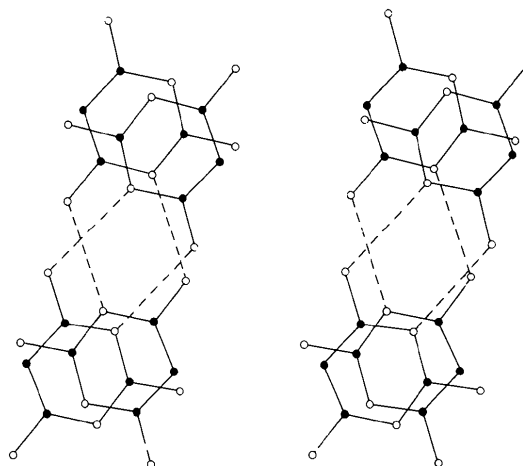


Fig. 3. A stereo-pair diagram showing the stacking interaction. The two upper molecules are related by a crystallographic inversion center, as are the two lower.

Each linear chain of hydrogen-bonded molecules is stacked against an equivalent chain. Fig. 3 illustrates a two-molecule fragment of this stacked double chain. Equivalent molecules are related by true inversion centers to stack against one another with a mean plane-to-plane separation of 3.43 (1) \AA .

We thank Professor C. J. Fritchie for helpful discussions, the Chemistry Department of Brookhaven National Laboratory for support for CHS, and the NIH for partial support of this work under grant GM24385.

References

- BAKER, B. R. & SANTI, D. V. (1965). *J. Pharm. Sci.* **54**, 1252–1257.

- BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.
- HUNT, W. E., SCHWALBE, C. H., BIRD, K. & MALLINSON, P. D. (1980). *Biochem. J.* **187**, 533–536.
- JOHNSON, C. K. (1976). *ORTEP-II*. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.
- KVICK, Á. & NOORDIK, J. (1977). *Acta Cryst.* **B33**, 2862–2866.
- ROGAN, P. K. & WILLIAMS, G. J. B. (1980). *Acta Cryst.* **B36**, 2358–2362.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- WILSON, A. J. C. (1942). *Nature (London)*, **150**, 151–152.

Acta Cryst. (1982). **B38**, 1843–1845

A Reinvestigation of the Structure of *N*-Dichloroacetyl-*S,S*-diethylsulphilimine

BY ALAJOS KÁLMÁN AND TIBOR KORITSÁNSZKY

Central Research Institute of Chemistry, Hungarian Academy of Sciences, H-1525 Budapest 114, POB 17, Hungary

AND ISTVÁN KAPOVITS AND ÁRPÁD KUCSMAN

Institute of Organic Chemistry, Eötvös University, H-1088 Budapest, Muzeum krt. 4/b, Hungary

(Received 4 August 1981; accepted 8 February 1982)

Abstract. $C_6H_{11}Cl_2NOS$, monoclinic, $P2_1/n$, $a = 6.950$ (1), $b = 11.322$ (1), $c = 12.460$ (2) Å, $\beta = 95.32$ (1)°, $V = 976.2$ (4) Å³, $Z = 4$, $D_c = 1.470$, $D_m = 1.468$ Mg m⁻³, $F(000) = 448$. The structure of Et₂SNCOCHCl₂, DEDAS, has been reinvestigated with diffractometer data. The atomic parameters obtained from film data ($R = 0.103$) have been refined by least squares to $R = 0.034$ for 2253 independent reflexions ($R_{tot} = 0.056$ for 2846 intensities). The S^{IV}–N bond length of 1.664 (1) Å and the S...O close contact of 2.838 (1) Å are discussed.

Introduction. A preliminary report on the X-ray structure determination of DEDAS was published (Kálmán, Sasvári & Kucsman, 1971) to confirm the conclusion obtained from IR (Kucsman, Ruff, Kapovits & Fischer, 1967; *cf.* Kucsman, Ruff & Tanács, 1976) and extended Hückel molecular-orbital (EHMO) studies (Mezey, 1970) that the S^{IV}–N bond is weaker in *N*-carbonylsulphilimines than in *N*-sulphonyl derivatives. The structure analysis of *S,S*-dimethyl-*N*-trichloroacetylsulphilimine (Me₂SNCOCCl₃, DMTAS; Kálmán, Sasvári & Kucsman, 1973) and that of *N*-benzoyl-*S,S*-dimethylsulphilimine [Me₂SN-COPh; DMBES; reported as *N*-benzoyliminosulphur(IV) by Cameron, Duncanson & Morris, 1976] have led to the same result. In all three *N*-carbonylsulphilimines the conjugated SNCO moiety is practically planar with the S and carbonyl O atoms being in *cis* arrangement. Since this conformation gives rise to an S...O close contact (Kálmán & Párkányi, 1980)

associated with a four-membered ring an accurate structure refinement of DEDAS was performed.

Experimental. The compound was recrystallized from methanol. A crystal 0.4 × 0.4 × 0.3 mm was mounted on an Enraf–Nonius CAD-4 computer-controlled diffractometer. The lattice parameters obtained from precession photographs were refined from the setting angles of 25 reflexions. 2846 independent intensities were collected with graphite-monochromated Mo *K*α ($\lambda = 0.71073$ Å) radiation. No absorption ($\mu = 0.91$ mm⁻¹) correction was performed.

Anisotropic refinement was started with the parameters obtained for non-hydrogen atoms in the first analysis ($R = 0.103$ for 963 Weissenberg observations). Full-matrix least-squares refinement of 101 variables reduced R to 0.053 for 2035 reflexions which were above the level $F - 10\sigma(F) > 0$. At this stage all H-atom positions could be located in a difference map. A further three cycles of least-squares adjustment in which H-atom positions were refined gave a final $R = 0.034$ ($R_w = 0.048$) for the 2253 reflexions with the $F - 6\sigma(F) > 0$ criterion ($R_{tot} = 0.056$)*. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). All calculations were per-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36680 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.