ly determined by packing requirements. The methoxypyridazine systems are packed nearly parallel to (0001) around a 3_1 axis at $\frac{1}{3},\frac{1}{3},z$ and the aniline groups, which are quite tilted with respect to (0001), are packed around a 3_2 axis at $\frac{1}{3},0,z$. The intermolecular distances less than 3·5 Å are given in Table 4.

Table 4. *Intermolecular distances*

Cl—N(4)	3·29 (2) Å	O(2)–N(2^{v})	3·08 (4) Å
Cl—Cl^{i}	3·48 (1)	O(3)–N(3^{iv})	3·30 (2)
Cl—O(1^{i})	3·31 (2)	O(3)–N(4^{iv})	3·22 (2)
O(1)–N(1^{ii})	3·10 (2)	O(3)–C(1^{iv})	3·34 (2)
O(1)–N(4^{ii})	2·73 (2)	O(3)–C(2^{iv})	3·50 (3)
O(1)–C(1^{ii})	3·37 (3)	O(3)–C(4^{iv})	3·39 (3)
O(1)–C(3^{iii})	3·28 (3)		

i	$\bar{y}$	$x-y$	z
ii	$y-x$	$\bar{x}$	z
iii	$y-x+\frac{1}{3}$	$\frac{2}{3}-x$	$z-\frac{1}{3}$
iv	$\bar{y}-\frac{1}{3}$	$x-y+\frac{1}{3}$	$z+\frac{1}{3}$
v	$\bar{y}+\frac{1}{3}$	$x-y+\frac{2}{3}$	$z+\frac{2}{3}$

The authors are indebted to Professor C. Cardani who suggested the research and to the Istituto De Angeli of Milan who kindly gave the crystals of the compound.

References

Adami, E., Piccinini, F. & Marazzi-Uberti, E. (1961). *Arzneim. Forsch.* (*Drug Res.*) **11**, 549.
Alléaume, M. & Decap, J. (1965). *Acta Cryst.* **18**, 731.
Atoji, M. & Watanabé, T. (1952). *J. Chem. Phys.* **20**, 1045.
Cavalca, L., Nardelli, M., Fava, G. & Giraldi, G. (1963). *Acta Cryst.* **16**, A69.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321.
Immirzi, A. (1967). *Ric. Sci.* **37**, 743.
Nardelli, M., Musatti, A., Domiano, P. & Andreetti, G. (1964). *Ric. Sci.* **34** (II-*A*), 711.
Nardelli, M., Musatti, A., Domiano, P. & Andreetti, G. (1965). *Ric. Sci.* **35** (II-*A*), 469, 477, 807.
O'Connor, B. H. & Maslen, E. N. (1965). *Acta Cryst.* **18**, 363.
Singer, J. & Fankuchen, I. (1952). *Acta Cryst.* **5**, 99.

Acta Cryst. (1972). B**28**, 1173

X-ray Studies of Pyridazino[4,5-*d*]pyridazine Derivatives. I. The Structure of 2,6-Dimethyl-4,8-dichloro-2*H*,6*H*-pyridazino[4,5-*d*]pyridazin-1,5-dione

By C. Sabelli
Centro di Geochimica e Cristallochimica dei Minerali del C.N.R., Istituto di Mineralogia dell'Università di Firenze, Italy

and P. F. Zanazzi
Istituto di Mineralogia dell'Università di Perugia, Italy

(*Received* 21 *September* 1971)

The crystal structure of 2,6-dimethyl-4,8-dichloro-2*H*,6*H*-pyridazino[4,5-*d*]pyridazin-1,5-dione (DDPPD) has been determined by a three-dimensional Patterson synthesis and refined by the method of least-squares to an R value of 0·075. The crystals of DDPPD are monoclinic, space group $P2_1/n$, with $a=9·189$, $b=5·546$, $c=10·230$ Å and $\beta=109·82°$; the cell content is $2C_8H_6N_4O_2Cl_2$. In the molecule of DDPPD the fused ring is approximately planar. Steric hindrance between Cl and O is responsible for the displacement of these atoms from the ring plane and for distortion of the molecule. The packing in the crystal is compact and explains the high melting point (320°C) of the compound.

Introduction

The structure determination on 2,6-dimethyl-4,8-dichloro-2*H*,6*H*-pyridazino[4,5-*d*]pyridazin-1,5-dione (DDPPD) was carried out as part of a programme on the derivatives of pyridazino[4,5-*d*]pyridazine (PP), a heterocyclic ring of very high symmetry, synthesized at the Istituto di Chimica Organica of Florence University (Adembri, De Sio, Nesi & Scotton, 1967). The study was undertaken in order to contribute to the knowledge of crystal and molecular structures of heterocyclic compounds with rings containing nitrogen atoms, and to investigate the packing of the molecules in crystals in this series of substances, with reference to the effect of different molecular substituents on the potential energy. The present paper follows one on the crystal structure of pyridazino[4,5-*d*]pyridazine (Sabelli, Tangocci & Zanazzi, 1969).

The results of the X-ray study on 1,4,5,8-tetramethoxypyridazino[4,5-*d*]pyridazine are reported in the following paper (Fanfani, Zanazzi & Sabelli, 1972).

Experimental

Crystals of DDPPD are obtained from benzene as yellowish needles, m.p. 319 to 321 °C (Adembri, De Sio, Nesi & Scotton, 1969).

DDPPD crystallizes in the monoclinic system; the unit-cell dimensions were determined from film data and refined by a least-squares method from the '*d*' values of high Bragg-angle reflexions, measured on *h*0*l* and 0*kl* Weissenberg photographs taken at room temperature and calibrated with Ag powder. They are

$$a = 9{\cdot}189\ (1)\ \text{Å}$$
$$b = 5{\cdot}546\ (2)$$
$$c = 10{\cdot}230\ (1)$$
$$\beta = 109{\cdot}82\ (2)^\circ.$$

The systematic absences in the diffraction pattern (*h*0*l* with $h+l$ odd; 0*k*0 with *k* odd) showed that the space group is $P2_1/n$. The calculated density (1·767 g.cm^{-3}, in agreement with that measured by flotation in a mixture of carbon tetrachloride and methylene iodide, 1·77 g.cm^{-3}) is consistent with the fact that there are two molecules of $C_8H_6N_4O_2Cl_2$ in the unit cell.

Diffraction data from 0*kl* to 5*kl* and from *h*0*l* to *h*4*l* reciprocal-lattice layers were collected with equi-inclination integrating Weissenberg apparatus using multiple-film techniques with Cu $K\alpha$ radiation. After the usual correction for Lorentz and polarization factors, the relative structure amplitudes were put on the same scale by comparison of the values of common reflexions in the 0*kl*–5*kl* and *h*0*l*–*h*4*l* sets. A total of 1024 independent data were collected; of these, 210 were too weak to be measured and were assigned an intensity value just below the observable intensity minimum. Absorption correction was neglected because of the small dimensions of the crystals used in obtaining the data.

Structure determination and refinement

The orientation of the DDPPD molecule, whose inversion centre must occupy the special position $\bar{1}$ of the space group, was determined by finding the positions of chlorine and oxygen atoms from the three-dimensional Patterson function. The atomic positions were better determined by successive electron density maps, until the value of the *R* index, defined as $\sum||F_o|-|F_c||/|F_o|$, was 0·26.

At this stage the least-squares refinement was undertaken with the full-matrix program of Busing and Levy, adapted for the IBM 7090 computer by Stewart (1964).* The weights assigned to the observed structure factors were $\sqrt{w}=1$ for reflexions with $F_o \le 4F_{\min}$; $\sqrt{w}=4F_{\min}/F_o$ for $F_o > 4F_{\min}$. Reflexions coded unobserved were given zero weights in the refinement if $F_c \le F_{\min}$; they were treated in the normal way if the calculated structure amplitudes were found greater in values than that corresponding to the observable intensity threshold. After two isotropic and two anisotropic cycles, the *R* index reduced to 0·088. At this stage a difference Fourier synthesis was computed, from which it was possible to locate the three hydrogen atoms of the methyl group in the asymmetric unit. The *R* index further reduced to 0·081. A cycle of refinement was then carried out for all atoms; thermal parameters of hydrogen atoms were set equal to 5 Å^2, and were not allowed to refine. This last cycle reduced the *R* value to 0·075. At this stage the refinement was stopped.

Final atomic coordinates and thermal parameters, together with the corresponding standard deviations, are shown in Tables 1 and 2. The observed and calculated structure factors are given in Table 3; the atomic scattering factors listed in *International Tables for X-ray Crystallography* (1962) for Cl, O, N, C and H were used for the calculations.

* The calculations were performed with the IBM 7090 computer of the Centro Nazionale di Calcolo Elettronico of Pisa University.

Table 1. *Fractional atomic coordinates with their e.s.d.'s in parentheses*

	x	*y*	*z*
Cl	0·1502 (2)	−0·3471 (2)	−0·1945 (1)
O	0·1468 (5)	0·4328 (7)	0·1651 (4)
N(1)	0·2587 (4)	0·1839 (7)	0·0550 (4)
N(2)	0·2612 (5)	−0·0017 (7)	−0·0299 (4)
C(1)	0·1364 (5)	0·2543 (9)	0·0952 (5)
C(2)	0·1367 (5)	−0·1304 (8)	−0·0781 (5)
C(3)	−0·0003 (5)	0·0930 (8)	0·0428 (4)
C(4)	0·4044 (6)	0·3179 (11)	0·1083 (6)
H(1)	0·485 (9)	0·260 (15)	0·057 (8)
H(2)	0·461 (9)	0·294 (14)	0·217 (8)
H(3)	0·365 (9)	0·497 (15)	0·092 (8)

Discussion of the structure

The structure of DDPPD projected along the *b* axis is shown in Fig. 1. Bond distances and angles with their e.s.d.'s are listed in Tables 4 and 5 and sketched in Fig. 2.

The heterocyclic ring is approximately planar; the equation of the mean-square plane through the four

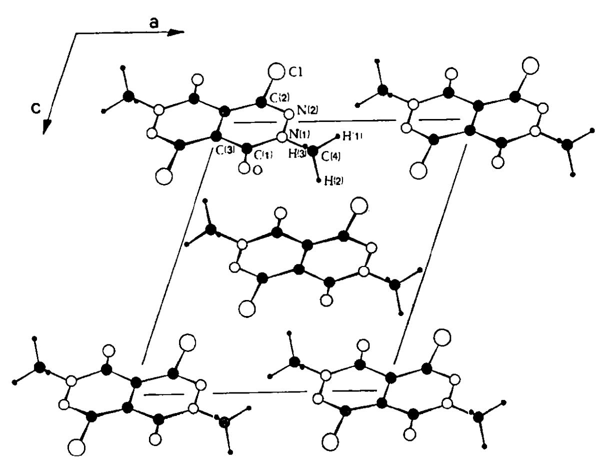


Fig. 1. The crystal structure of DDPPD projected along [010].

nitrogen and the six carbon atoms of the fused ring is:

$$-0{\cdot}858x+3{\cdot}313y-7{\cdot}341z=0$$

where x, y and z are the fractional atomic coordinates referred to the monoclinic cell axes. The displacements Δ of the non-hydrogen atoms from this plane are listed in Table 6. The maximum displacement for the ring atoms is 0·027 Å. The methyl group is out of the plane by 0·089 Å; the adjacent oxygen and chlorine atoms are displaced from the plane in opposite directions: oxygen by 0·096 Å and chlorine by 0·149 Å.

Table 2. *Thermal parameters with e.s.d.'s in parentheses*

For non-hydrogen atoms the β_{ij} coefficients of the expression

$$\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right]$$

are listed ($\times 10^4$). For hydrogen atoms the isotropic B values (Å^2) are given.

	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	152 (1)	325 (5)	129 (1)	−8 (2)	72 (1)	−66 (2)
O	176 (7)	352 (19)	176 (5)	−51 (9)	79 (5)	−94 (9)
N(1)	112 (6)	270 (17)	94 (4)	−29 (8)	34 (4)	−6 (7)
N(2)	122 (6)	262 (16)	89 (4)	−4 (8)	39 (4)	−3 (7)
C(1)	127 (8)	253 (17)	96 (6)	−15 (10)	36 (6)	−2 (10)
C(2)	122 (7)	247 (18)	86 (5)	2 (10)	40 (5)	−8 (8)
C(3)	122 (7)	226 (17)	80 (5)	13 (9)	33 (5)	8 (8)
C(4)	120 (8)	342 (22)	136 (7)	−42 (11)	36 (6)	−14 (11)
H(1)	5					
H(2)	5					
H(3)	5					

Table 3. *Observed and calculated structure factors* ($\times 10$)

The asterisk designates the unobserved reflexions.

[illegible]

Table 4. *Bond distances with their e.s.d.'s in parentheses*

	Uncorrected values	Corrected for angular oscillation
Cl—C(2)	1·726 (5) Å	1·730 Å
C(2)–N(2)	1·296 (6)	1·299
N(2)–N(1)	1·352 (6)	1·359
N(1)–C(4)	1·465 (7)	1·469
N(1)–C(1)	1·378 (6)	1·379
C(1)–O	1·205 (6)	1·209
C(1)–C(3)	1·486 (6)	1·489
C(3)–C(3′)	1·354 (12)	1·361
C(3′)–C(2)	1·433 (6)	1·435
C(4)–H(1)	1·09 (8)	
C(4)–H(2)	1·06 (8)	
C(4)–H(3)	1·05 (8)	

Table 5. *Bond angles with their e.s.d.'s in parentheses*

N(1)–C(1)–C(3)	113·4 (4)°
N(1)–C(1)–O	120·1 (4)
O—C(1)–C(3)	126·6 (4)
C(1)–C(3)–C(3′)	120·3 (4)
C(1)–C(3)–C(2′)	121·8 (4)
C(3)–C(3′)–C(2)	117·9 (4)
C(3′)–C(2)–N(2)	124·0 (4)
C(3′)–C(2)–Cl	123·3 (3)
C(2)–N(2)–N(1)	117·3 (4)
N(2)–C(2)–Cl	112·7 (3)
N(2)–N(1)–C(1)	127·0 (4)
C(4)–N(1)–N(2)	114·4 (4)
C(4)–N(1)–C(1)	118·7 (4)
H(1)–C(4)–N(1)	111 (4)
H(2)–C(4)–N(1)	113 (4)
H(3)–C(4)–N(1)	101 (4)
H(1)–C(4)–H(2)	107 (6)
H(1)–C(4)–H(3)	117 (6)
H(2)–C(4)–H(3)	107 (6)

Table 6. *Deviations of atoms from least-squares plane*

Cl	0·149 Å	C(1)	0·027 Å
O	0·096	C(2)	0·024
N(1)	−0·016	C(3)	−0·006
N(2)	−0·011	C(4)	−0·089

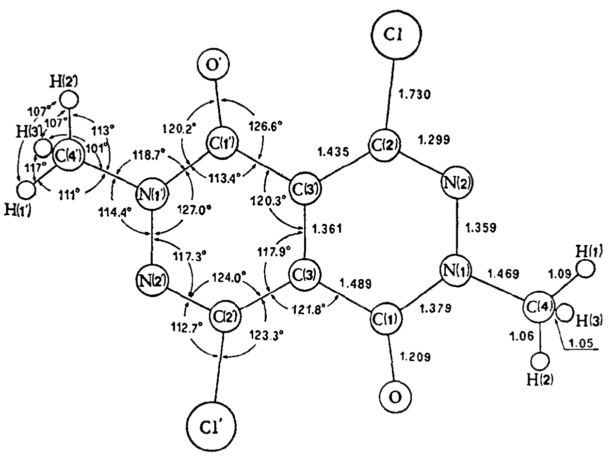
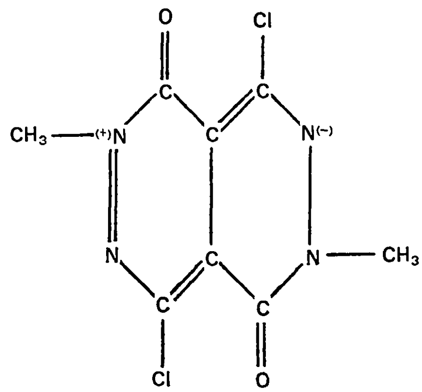


Fig. 2. Bond distances (Å) and angles in the molecule.

This fact, as well as the in-plane splaying apart of C–Cl and C–O bonds by about 3 and 7° respectively, is due to the effect of steric hindrance, the resulting distance Cl–O being 2·885 Å. Because of this interaction there is a partial hindrance to conjugation in the system O′=C(1′)–C(3′)=C(3)–C(1)=O shown by shifts in the C=O 'stretching' frequency (observed in DDPPD at $\nu=1675$ cm^{-1}) with respect to the frequency measured in the non-halogenated 2,6-dimethyl-2*H*,6*H*-pyridazino[4,5-*d*]pyridazin-1,5-dione ($\nu=1645$ cm^{-1}, Adembri, De Sio, Nesi & Scotton, private communication). From considerations of bond distances and angles, a mesomeric form of the type



seems favoured. This could account for the shortening of the C(2)–C(3′) bond (1·435 Å) with respect to the C(1)–C(3) bond (1·489 Å), and for the shortening of the distance between the two nitrogen atoms to a value (1·359 Å) between a single and a double N–N bond and shorter than the homologous distance in PP (1·382 Å). Furthermore, this conjugative effect may explain the values of the bond angles around the N(1) atom, nearer to those expected for the sp^2 hybridization than

Table 7. *Shortest intermolecular distances*

O—C(2)	x	$\frac{1}{2}+y$	z	3·451 Å
H(2)–C(2)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	2·860
O—O				3·474
O—N(1)				3·035
O—C(1)				3·138
H(2)–C(3)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	2·885
O—C(4)				3·301
O—H(2)				2·699
N(2)–Cl	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$-\frac{1}{2}-z$	3·303
H(2)–Cl	$\frac{1}{2}+x$	$-\frac{1}{2}-y$	$\frac{1}{2}+z$	2·986
Cl—Cl	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$-\frac{1}{2}-z$	3·709

Table 8. *Values of* T_{ij} (10^{-2} Å^2) *and* ω_{ij} (10^{-2} rad^2)

$$\mathbf{T}=\begin{bmatrix} 3.93 & -0.38 & 0.07 \\ & 3.90 & -0.28 \\ & & 3.36 \end{bmatrix}$$

$$\boldsymbol{\omega}=\begin{bmatrix} 0.41 & -0.32 & 0.01 \\ & 0.27 & 0.00 \\ & & 0.15 \end{bmatrix}$$

Table 9. *Observed and calculated* U_{ij} (10^{-2} Å^2)

	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
Cl	3·41	3·99	5·18	5·56	7·50	7·90	−0·71	−0·71	0·21	0·06	−0·27	−0·24
O	5·17	5·02	4·83	4·15	9·80	8·99	−0·94	−0·90	−0·15	0·00	−0·69	−0·25
N(1)	4·76	4·73	3·57	4·02	4·56	4·44	0·05	−0·07	0·25	0·03	−0·22	−0·30
N(2)	4·19	4·28	4·30	4·51	4·27	3·49	−0·22	0·08	0·18	0·06	−0·19	−0·30
C(1)	4·82	4·46	4·08	3·92	4·40	5·33	−0·31	−0·49	0·04	0·04	−0·34	−0·27
C(2)	3·81	3·94	4·31	4·41	4·21	4·04	−0·39	−0·32	0·12	0·07	−0·19	−0·28
C(3)	4·02	3·96	4·43	3·94	3·46	3·65	−0·45	−0·41	−0·09	0·07	−0·19	−0·28
C(4)	6·23	6·04	3·92	4·11	6·36	6·69	0·43	0·29	−0·29	−0·04	−0·14	−0·32

to the tetrahedral values of an sp^3 hybridization. The shortening of the N(1)–N(2) bond length is also consistent with the effect that one would expect the overcrowding of chlorine and oxygen atoms to have on the ring. It is interesting to observe this effect in other compounds with bulky substituents, for example in 1,4,5,8-tetrachloronaphthalene (Gafner & Herbstein, 1962).

By comparing the bond lengths of DDPPD with those found in 'aromatic' PP, it is evident that in DDPPD there is a minor delocalization of the charge. The C(3)–C(3′) and N(2)–C(2) distances, 1·361 and 1·299 Å respectively, are nearer to carbon–carbon and nitrogen–carbon double bond values found in the literature than in PP, where the analogous distances are 1·388 and 1·312 Å. However, the bond lengths C(2)–C(3′), C(1)–C(3) and N(1)–C(1) are nearer to accepted single-bond values in DDPPD than in PP.

The packing of DDPPD molecules in the crystal is compact and explains the high melting point, 320 °C, of the compound. The shortest intermolecular contacts, which are significant with respect to the sum of van der Waals radii for Cl, O, N, C and H, are listed in Table 7.

The thermal motion of DDPPD molecules was analysed in terms of 'rigid-body' motion, according to the method of Cruickshank (1956). The **T** and **ω** tensors, and the observed and calculated **U** tensors are listed in Tables 8 and 9 respectively. They are referred to a system of orthogonal molecular axes X, Y, Z. The direction cosines of the X, Y and Z axes, referred to the crystallographic axes, are

X	−0·7516	0·4825	0·6781
Y	0·6530	0·6406	0·1589
Z	−0·0934	0·5973	−0·7176 .

These axes are those which reduce the moment-of-inertia tensor of the molecule to diagonal form.

A correction to bond lengths and angles for libration was computed according to the method of Cruickshank (1961) and assuming a shape parameter $q^2 = 0·12$. The corrections in bond angles are negligible (less than $\frac{1}{2}\sigma$, *i.e.* 0·2°). The corrections on bond lengths are small (maximum value is 7×10^{-3} Å, equal to about 1σ). Corrected values are listed in Table 4.

The authors wish to thank Professors G. Adembri, F. De Sio, R. Nesi and M. Scotton of the Istituto di Chimica Organica of Florence University for providing the sample and for the helpful discussions. This work was made possible through financial support of the Consiglio Nazionale delle Ricerche, Roma.

References

ADEMBRI, G., DE SIO, F., NESI, R., & SCOTTON, M. (1967). *Chem. Commun.* p. 1006.

ADEMBRI, G., DE SIO, F., NESI, R., & SCOTTON, M. (1969). *2ème Congrès Int. de Chimie Heterocyclique,* Montpellier, p. 188.

CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.

CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896.

FANFANI, L., ZANAZZI, P. F. & SABELLI, C. (1972). *Acta Cryst.* **B28**, 1178.

GAFNER, G. & HERBSTEIN, F. H. (1962). *Acta Cryst.* **15**, 1081.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202, Birmingham: Kynoch Press.

SABELLI, C., TANGOCCI, P. & ZANAZZI, P. F. (1969). *Acta Cryst.* **B25**, p. 2231.

STEWART, J. M. (1964). Technical Report TR-64-6, Computer Science Center, Univ. of Maryland.