nating properties of $SeCl_4$ (Groeneveld, 1953). The observed Al–Cl distances (average 2·13 Å) in this structure agree very well with those ($\sim$2·14 Å) found in $AlCl_4^-$ ions in the compound $Mg(CH_3CN)_6(AlCl_4)_2$ (Stork-Blaisse & Romers, 1971). Al is coordinated octahedrally in $AlCl_3$ and accordingly the Al–Cl distances are larger ($\sim$2·31 Å) (Ketelaar *et al.* 1947).

All calculations were performed on the IBM 360/50 computer with programs developed by Mrs E. W. M. Rutten (Fourier and least-squares) and by Mr R. A. G. de Graaff (geometry). The authors thank Dr Groeneveld for his supply of crystals. They are indebted to Mr R. Ch. D. E. Hasekamp and Mr J. C. Portheine for the production of the diffraction photographs.

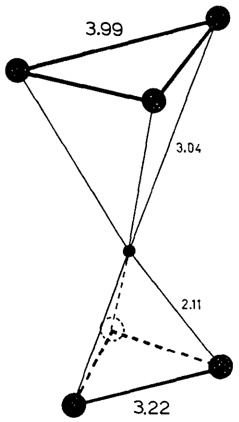

Fig. 3. Idealized deformed octahedron with C_{3v} symmetry. The distances shown (Å) are mean values of the two octahedra.

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The Crystal and Molecular Structure of a Sulphur-Containing Antibiotic, 'vD844', 5-Oxo-6-*N*-methylformylamino-4,5-dihydro-1,2-dithiolo[4,3-*b*] pyrrole

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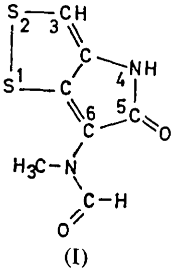
The antibiotic 5-oxo-6-*N*-methylformylamino-4,5-dihydro-1,2-dithiolo[4,3-*b*]pyrrole, $C_7H_6N_2O_2S_2$, crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 14{\cdot}22$, $b = 3{\cdot}788$, $c = 19{\cdot}06$ Å; $\beta = 116{\cdot}4°$. The unit cell also contains about 3 molecules of water. The structure was solved from two- and three-dimensional Patterson syntheses and refined by the full-matrix least-squares method, producing a final R value of 0·105. It shows some disorder, caused partly by the water molecules and partly by the presence of two different conformations of the vD844 molecule in the crystal. The ring system is approximately planar and the side chain is twisted about 42° out of this plane, the angle being approximately the same in both of the conformations of the vD844 molecule. N–H---O hydrogen bonds of length 2·83 Å connect the vD844 molecules in pairs. The positions of the water molecules are not well defined; the molecular packing is very compact and leaves sufficient space for only about three of any four equivalent positions to be occupied. The average distance found between the oxygen atoms of two water molecules is 2·34 Å.

Introduction

A compound with anti-bacterial activity, and called vD844, has been separated from the culture fluid of an unidentified *Streptomyces* species isolated from a soil sample collected near Copenhagen. It is strongly active against *Neisseria* and certain other gram-negative organisms, but it is rather toxic. Chemical investigations of the compound have been made by von Daene, Godtfredsen, Tybring & Schaumburg (1969) who propose the formula 5-oxo-6-*N*-methylformylamino-4,5-dihydro-1,2-dithiolo[4,3-*b*]pyrrole (I) for it.



(I)

This communication describes the unambiguous determination of the molecular structure of vD844 using single-crystal X-ray diffraction techniques. A preliminary communication on this investigation has been published (Jensen, 1969).

Experimental and crystal data

Crystals of vD844, which were kindly provided by Dr W. O. Godtfredsen, Leo Pharmaceutical Products, Ballerup, Denmark, grow slowly at the interface between ethyl acetate and water. They are yellow, monoclinic needles elongated in the **b** direction; m.p. 181–182°C. X-ray diffraction photographs of them indicate some structural disorder. Two types of reflexions are seen: the first is a class of sharp, normally strong reflexions which alone correspond to a structure with space group $P2_1/c$ and unit-cell dimensions $a=14{\cdot}22\pm0{\cdot}03$, $b=3{\cdot}788\pm0{\cdot}004$, $c=19{\cdot}06\pm0{\cdot}04$ Å, $\beta=116{\cdot}4\pm0{\cdot}3°$; between these a second class, consisting of weak, diffuse reflexions, is observed. The average intensity of these diffuse reflexions is about one half of the minimum observed intensity for the sharp reflexions. Consideration of these reflexions leads to the space group Cc or $C2/c$ and doubling of the a and b axes. However, for reasons discussed below the analysis was based on the sharp reflexions only, so that remarks in this paper will always refer to the space group $P2_1/c$ and the smaller unit-cell. The density of $1{\cdot}63\pm0{\cdot}02$ g.cm^{-3} measured by flotation in a mixture of CCl_4 and C_2H_5I shows a great deviation from the density of 1·56 g.cm^{-3} calculated for 4 molecules of vD844 having the structure proposed by von Daene, Godtfredsen, Tybring & Schaumburg (1969) and indicates an additional content of approximately 50 a.m.u. per unit cell. That this is due to about 3 molecules of water of crystallization has been confirmed by elementary analysis and by the structure determination. The density calculated on this basis is 1·64 g.cm^{-3}.

According to Eisenman, Minieri, Abbey, Carlebois, Moncrieff-Yeates & Rigler (1953), the antibiotic HA–9, which is apparently identical with vD844, forms small, probably orthorhombic, crystals from benzene. A few attempts to prepare anhydrous crystals, limited by the small amount of compound available, were made, but without success.

X-ray diffraction photographs from several crystals were taken, and all show the same pattern, even those from specimens of vD844 recrystallized from ethanol. All the X-ray data used for intensity measurements were registered from a needle with the dimensions $0{\cdot}14\times0{\cdot}1\times0{\cdot}55$ mm. Using Cu $K\alpha$ radiation and Weissenberg equi-inclination techniques, multiple-film exposures were taken of the layers $0\le k\le3$ and of the two weak, diffuse layers with $k=$ '$\frac{1}{2}$' and '$\frac{3}{2}$' respectively. Precession photographs of $hk0$, $0kl$ and $1kl$ were also taken with Mo $K\alpha$ radiation. The intensities of all the reflexions were estimated visually, corrected for geometrical factors, including corrections due to spot shape variations (Phillips, 1956) and scaled to produce a total of 965 sharp and 527 diffuse non-zero reflexions. Data measured from the precession photographs were used in the data scaling to correlate the Weissenberg-recorded observations but were not included in the final data set. The number of sharp reflexions observed corresponds to about 52% of that theoretically attainable with copper radiation. No corrections for extinction or absorption were applied (linear absorption coefficient, μCu $K\alpha=30{\cdot}6$ cm^{-1}).

Determination and refinement of the structure

Because of the very short b axis, the x and z parameters of most non-hydrogen atoms were easily deduced from the Patterson synthesis, $P(xz)$, using the minimum function (Buerger, 1959). The inversion peaks corresponding to the two sulphur atoms were found, and by combination of the two $M_2(xz)$ maps for these peaks an $M_4(xz)$ map was obtained from which the coordinates of the atoms of the greater part of the molecule could be postulated. An electron density projection, $\varrho(xz)$, phased on the contributions of these atoms to the structure factors, showed the whole molecule clearly. After a single cycle of R minimization (Bhuiya & Stanley, 1963) using an ALGOL program written by Danielsen,* the $R(h0l)$ value was 0·28.

The y parameters were subsequently found from the three-dimensional Patterson synthesis, $P(xyz)$, calculated from the sharp reflexions.

The disorder in the structure had thus far been neglected. An electron density projection $\varrho(xz)$ calculated at this stage is shown in Fig. 1, and shows two features which can be interpreted to lead to the presence of the weak, diffuse reflexions observed. (1) Two peaks (indicated by arrows) are situated in positions which correspond to those expected for the oxygen atom in the formylamino group of the side chain in each of two orientations. Both appear with peak heights about one half of that expected for an oxygen peak. Thus the

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vD844 molecules appear to be present in two conformations in the crystal and the electron density map shows a superposition of the two. (2) The peaks near $(\frac{1}{2},\frac{1}{4})$ correspond to the oxygen atoms of water molecules with only about 75% occupancy of the 4 equivalent positions in the unit cell.

As none of the distances from the water oxygen atom positions to the atoms in the side chains is shorter than the sums of the respective van der Waals radii, a connection between the two kinds of disorder seemed improbable. In an attempt to determine the nature of the irregularities the following postulates were tested. (1) The ring system of the vD844 molecules can be completely described in the space group $P2_1/c$; and the difference in conformation of the vD844 molecules is regular so that their packing alone corresponds

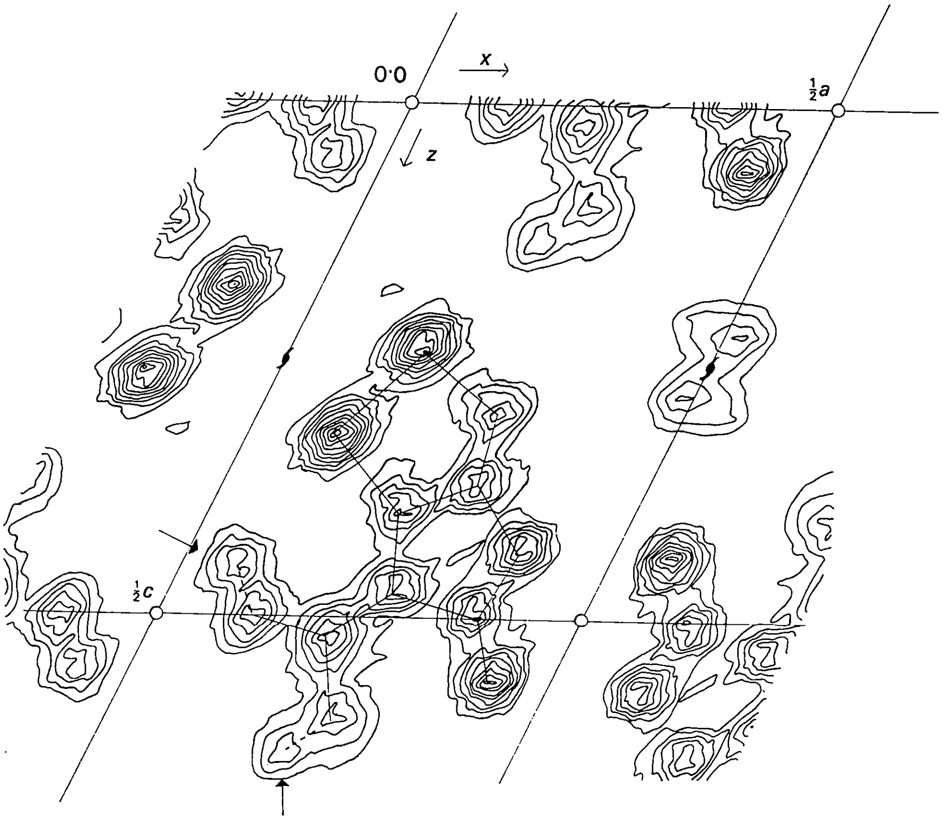

Fig. 1. Electron density projection on (010). The contour levels are on an arbitrary scale. Two peaks (indicated by arrows) are situated in positions corresponding to disordered formyl oxygen atoms, and indicate the presence of two conformations of the vD844 molecules in the crystal.

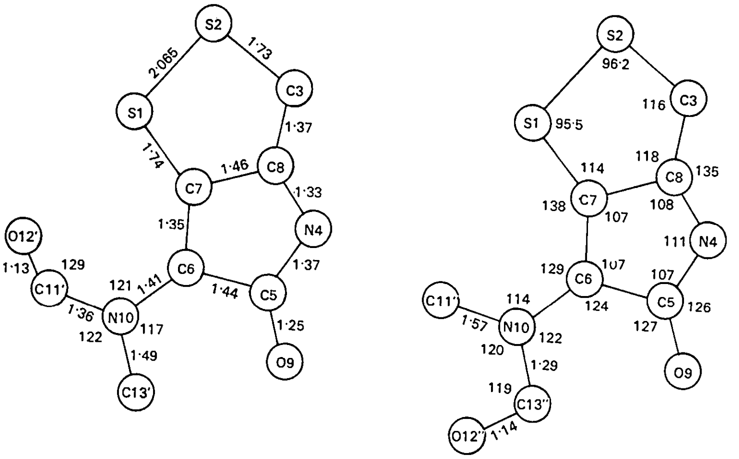

Fig. 2. Bond distances (Å) and angles (°).

Table 1. *Final atomic parameters*

Anisotropic parameters are of the form exp $[-\frac{1}{4}(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+2hka^*b^*B_{12}+2hla^*c^*B_{13}+2klb^*c^*B_{23})]$. *M* is the site occupancy factor

	x/a	*y/b*	*z/c*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	*M*
S(1)	0·1037 (2)	1·0843 (7)	0·3210 (2)	2·6 (1)	2·7 (1)	3·7 (1)	0·8 (1)	−0·3 (1)	−0·8 (1)	
S(2)	0·1509 (2)	1·0651 (8)	0·2332 (2)	3·6 (1)	3·5 (2)	3·1 (1)	−0·4 (1)	−0·2 (1)	1·3 (1)	
C(3)	0·2759 (9)	0·9080 (30)	0·2908 (6)	4·5 (5)	3·8 (6)	2·8 (4)	−1·5 (4)	0·2 (4)	−0·7 (4)	
N(4)	0·3847 (5)	0·7267 (20)	0·4290 (4)	2·3 (3)	2·1 (4)	2·8 (3)	0·8 (3)	1·0 (3)	0·1 (2)	
C(5)	0·3668 (6)	0·7141 (23)	0·4937 (5)	2·2 (3)	2·1 (4)	2·3 (3)	0·4 (3)	1·0 (3)	0·0 (3)	
C(6)	0·2611 (7)	0·8379 (22)	0·4701 (5)	2·7 (4)	0·9 (4)	3·2 (4)	−0·4 (3)	0·8 (3)	−0·5 (3)	
C(7)	0·2204 (7)	0·9200 (25)	0·3935 (5)	2·6 (3)	2·3 (4)	2·6 (4)	0·9 (3)	0·4 (3)	0·3 (3)	
C(8)	0·3001 (6)	0·8414 (21)	0·3675 (5)	2·1 (3)	0·5 (3)	3·0 (4)	−0·2 (2)	0·2 (3)	−0·5 (2)	
O(9)	0·4285 (5)	0·5935 (18)	0·5588 (4)	2·7 (3)	3·8 (3)	2·4 (2)	0·2 (2)	0·9 (2)	0·4 (2)	
N(10)	0·2140 (6)	0·8642 (22)	0·5209 (5)	2·7 (3)	3·0 (4)	4·0 (4)	−0·0 (3)	1·5 (3)	−0·4 (3)	
C(11′)	0·1152 (15)	0·7416 (67)	0·5001 (12)	0·5 (6)	4·8 (16)	3·7 (10)	0·5 (8)	−0·9 (6)	2·0 (10)	0·50 (5)
C(11″)	0·0931 (26)	0·7855 (78)	0·4805 (30)	2·7 (18)	5·3 (18)	8·3 (28)	1·3 (12)	3·1 (20)	−0·9 (19)	0·51 (5)
O(12′)	0·0542 (12)	0·6500 (60)	0·4411 (11)	4·4 (7)	9·0 (17)	7·3 (11)	−0·1 (9)	2·8 (8)	1·3 (10)	0·64 (4)
O(12″)	0·2183 (15)	1·0458 (40)	0·6254 (9)	10·7 (14)	7·4 (11)	6·9 (11)	0·8 (9)	6·4 (10)	0·2 (8)	0·63 (4)
C(13′)	0·2827 (15)	0·9824 (48)	0·6019 (9)	3·9 (10)	1·3 (13)	1·9 (9)	1·9 (7)	0·7 (7)	1·2 (7)	0·55 (3)
C(13″)	0·2537 (24)	1·0581 (59)	0·5824 (15)	6·4 (22)	2·0 (13)	3·1 (13)	3·5 (11)	2·6 (15)	1·8 (9)	0·44 (3)
O(14)	0·5016 (21)	1·0327 (59)	0·7860 (9)	18·2 (19)	15·7 (17)	4·9 (8)	8·7 (14)	3·9 (11)	0·7 (9)	0·80 (3)

to *Cc* symmetry, and only the water molecules are really disordered and cause the weak reflexions to be diffuse. (2) The vD844 molecules occupying only one equivalent position may have different conformations and these may give rise to small displacements of the neighbouring molecules and thereby cause all of them to contribute to the disorder. (3) The ring systems have practically fixed positions and both the side chains and the water molecules contribute to the disorder.

Postulate (1) was rejected for the following reason. The asymmetric unit in space group *Cc* will contain 4 molecules of vD844 and 3 molecules of water, and the vD844 molecules should differ from each other only in the conformation of the side chain. Attempts were made to postulate an ordered structure in space group *Cc*, but none of the possible combinations of vD844 molecules having different conformations produced the intensity distribution of the diffuse diffraction pattern; and all calculated Fourier syntheses showed peaks corresponding to a formyl oxygen atom in each of the two conformers in all the four vD844 molecules in the asymmetric unit. As stated later in this paper (see *Discussion*) an ordered distribution of the vD844 molecules of different conformation is not too likely.

If postulate (2) were true exceptional 'thermal vibrations' for all atoms in the structure would have been expected. But the anisotropic motion actually found is normal for the greater part of the vD844 molecule, and could not give rise to the observed disorder effects. (2) was therefore abandoned.

Postulate (3) was then accepted. The refinement of the structure was made assuming space group $P2_1/c$, and only the sharp reflexions were included. Attempts to explain the intensity distribution of the weak diffuse zones have not been made.

The refinement was performed by the full-matrix least-squares method. Positional parameters for all atoms, including those corresponding to both possible side chain orientations and the postulated water oxygen atom, were refined in all cycles. Site occupancy factors for the disordered atoms were also refined. In the first three cycles individual atomic isotropic temperature factors were assumed, but these were extended to anisotropic parameters for the next four cycles. Finally four scale factor parameters, each corresponding to a layer of observed data, were varied. To avoid the possible occurrence of matrix singularities, some thermal parameters (but not the same parameters for all cycles) were held fixed. The data weighting scheme was that proposed by Hughes (1941), and no unobserved reflexions were included in the calculations. The scattering factors were taken from *International Tables for X-ray Crystallography* (1962). After the last cycle all shifts were less than one third of their corresponding estimated standard deviations. The final reliability index, *R*, is 0·105. Table 6 lists the observed structure amplitudes and the corresponding calculated structure factors from the final structural parameters. After the refinement a difference Fourier synthesis was calculated, but it was not possible to establish the positions of the hydrogen atoms in the structure from this with any reasonable certainty.

Most of the calculations were performed on the IBM 7090 and 7094 computers at Northern Europe University Computing Center, Lyngby, Denmark, using the integrated program system *X-Ray* 63 from the University of Maryland (Stewart, 1964).

Description and discussion of the structure

The bond lengths and angles and their corresponding estimated standard deviations, calculated from the final atomic coordinates in Table 1, are given in Tables 2 and 3 and Fig. 2, and a list of interatomic distances describing the surroundings of the sulphur atoms, the formyl-oxygen atoms and the water oxygen atom is given in Table 4. The least-squares planes, *A*, *B* and *C*, through N(4), C(5), C(6), C(7) and C(8), through C(6), N(10), C(11′), O(12′) and C(13′) and through C(6), N(10), C(11″), O(12″) and C(13″), respectively, were calculated. The parameters of these planes, the deviations of the atoms from them and the angles between them are given in Table 5.

Table 2. *Bond lengths, with their e.s.d.'s* ($\times 10^3$) *in parentheses*

Distances between atoms probably not belonging to the same conformation of the vD844 molecule are marked with an asterisk.

S(1)—S(2)	2·065 (5) Å
S(2)—C(3)	1·728 (11)
C(3)—C(8)	1·371 (15)
C(8)—C(7)	1·455 (16)
C(7)—S(1)	1·736 (8)
C(8)—N(4)	1·327 (9)
N(4)—C(5)	1·368 (14)
C(5)—C(6)	1·442 (13)
C(6)—C(7)	1·351 (13)
C(5)—O(9)	1·248 (9)
C(6)—N(10)	1·406 (16)
N(10)—C(11′)	1·361 (23)
C(11′)-O(12′)	1·130 (25)
N(10)—C(13′)	1·485 (17)
N(10)—C(11″)	1·567 (33)
C(13″)-O(12″)	1·137 (43)
N(10)—C(13″)	1·286 (25)
C(11″)-O(12′)	0·877 *(43)
C(13′)-O(12″)	1·208 *(33)
C(11′)-C(11″)	0·402 (42)
C(13′)-C(13″)	0·505 (28)

Table 3. *Bond angles, with their e.s.d.'s in parentheses*

Angles including atoms probably belonging to different conformations of the vD844 molecules are marked with an asterisk.

S(1)—S(2)—C(3)	96·2 (0·5)°
S(2)—C(3)—C(8)	116·3 (1·0)
C(3)—C(8)—C(7)	117·6 (0·8)
C(8)—C(7)—S(1)	114·4 (0·7)
C(7)—S(1)—S(2)	95·5 (0·4)
C(3)—C(8)—N(4)	134·9 (1·1)
C(7)—C(8)—N(4)	107·5 (0·8)
C(8)—N(4)—C(5)	110·6 (0·8)
N(4)—C(5)—C(6)	107·0 (0·7)
N(4)—C(5)—O(9)	125·6 (0·9)
C(6)—C(5)—O(9)	127·1 (1·0)
C(5)—C(6)—C(7)	107·4 (1·0)
C(6)—C(7)—C(8)	107·4 (0·8)
S(1)—C(7)—C(6)	138·2 (0·9)
C(7)—C(6)—N(10)	128·8 (0·9)
C(5)—C(6)—N(10)	123·9 (0·8)
C(6)—N(10)—C(11′)	121·4 (1·2)
N(10)—C(11′)-O(12′)	129·0 (2·5)
C(6)—N(10)—C(13′)	116·5 (1·1)
C(11′)-N(10)—C(13′)	121·5 (1·5)
C(6)—N(10)—C(11″)	113·6 (2·2)
C(6)—N(10)—C(13″)	121·5 (1·8)
N(10)—C(13″)-O(12″)	118·8 (2·6)
C(11″)-N(10)—C(13″)	119·9 (2·6)
N(10)—C(11″)-O(12′)	132·0 *(4·9)
N(10)—C(13′)-O(12″)	101·1 *(1·4)
C(11′)-N(10)—C(13″)	116·0 *(2·1)
C(11″)-N(10)—C(13′)	129·7 *(2·4)

Table 4. *Interatomic distances describing the surroundings of the sulphur atoms, the formyl oxygen atoms and the water oxygen atom*

General equivalent positions of the molecules are:

I	(x, y, z)	VI	$(x, 2\frac{1}{2}-y, \frac{1}{2}+z)$
II	$(-x, y-\frac{1}{2}, \frac{1}{2}-z)$	VII	$(x, 1\frac{1}{2}-y, \frac{1}{2}+z)$
III	$(-x, 2-y, 1-z)$	VIII	$(x, y+1, z)$
IV	$(-x, 1-y, 1-z)$	IX	$(1-x, y+\frac{1}{2}, 1\frac{1}{2}-z)$
V	$(x, y-1, z)$	X	$(1-x, y-\frac{1}{2}, 1\frac{1}{2}-z)$

From atom		to atom		
S(1)	I	S(2)	II	3·84 Å
S(1)	I	S(1)	II	3·54
S(2)	I	S(1)	II	3·76
O(12′)	I	O(12″)	III	3·68
O(12′)	I	C(11′)	III	3·85
O(12′)	I	C(11″)	III	3·74
O(12′)	I	O(12′)	III	4·19
O(12′)	I	O(12″)	IV	4·38

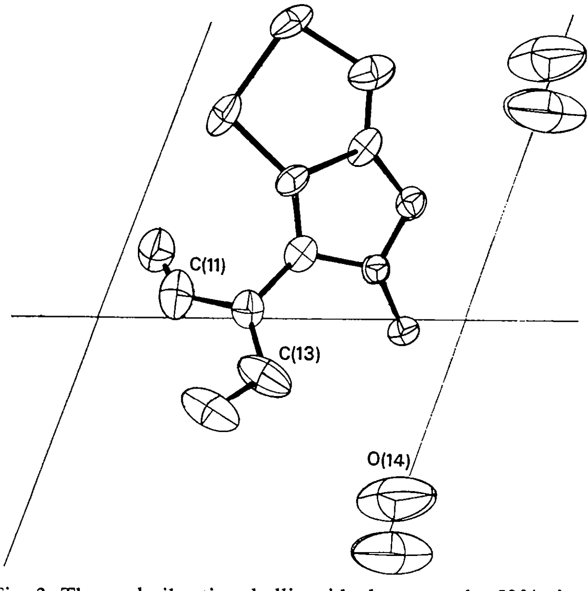

Fig. 3. Thermal vibrational ellipsoids drawn at the 50% significance level. C(11) and C(13) are shown as one atom each, not as the fractional atoms mentioned in the paper.

Table 4 (*cont.*)

From atom	to atom	
O(12′) I	C(11′) IV	3·42
O(12′) I	C(11″) IV	3·49
O(12′) I	O(12′) IV	3·44
O(12′) I	O(12″) V	3·98
O(12′) I	N(10) V	3·65
O(12′) I	C(11′) V	3·61
O(12′) I	C(11″) V	3·36
O(12′) I	S(1) I	3·15
O(12″) I	S(2) VI	3·02
O(12″) I	C(3) VI	3·56
O(12″) I	S(2) VII	3·51
O(12″) I	C(3) VII	3·37
O(12″) I	C(13′) VIII	3·75
O(12″) I	C(13″) VIII	4·01
O(12″) I	N(10) VIII	3·68
O(12″) I	C(11′) VIII	3·43
O(12″) I	C(11″) VIII	3·79
O(14) I	C(13′) IX	3·33
O(14) I	C(13″) IX	3·82
O(14) I	O(12″) IX	4·06
O(14) I	O(9) IX	2·69
O(14) I	O(14) IX	2·33
O(14) I	C(13′) X	3·54
O(14) I	C(13″) X	3·73
O(14) I	O(12″) X	4·02
O(14) I	C(13′) I	3·52
O(14) I	C(13″) I	3·92
O(14) I	O(12″) I	3·83

The deviations of all the ring atoms and of N(10) from plane *A* are small and not significant, and the bond lengths in the ring system are as expected for a planar system with conjugated double bonds. The S–S distance of 2·07 Å indicates definitely a single bond,

Table 5. *Least-squares planes and the angles between them*

The equations of the planes are in orthogonal Å space (**I** parallel to **a**; **J** parallel to **b** and **K** parallel to **c***) and the distances of the atoms from the least-squares planes are in Å.

Distances to atoms defining the plane are asterisked.

$A\ 0{\cdot}26902I+0{\cdot}93571J+0{\cdot}22820K-4{\cdot}7401\ =0$

$B\ 0{\cdot}20409I-0{\cdot}93268J+0{\cdot}29741K+0{\cdot}64812=0$

$C\ 0{\cdot}11601I-0{\cdot}91997J+0{\cdot}37443K-2{\cdot}1666\ =0$

$\angle$ plane A plane B 41°

$\angle$ plane A plane C 42°

$\angle$ plane B plane C 7°

Atom	*A*	*B*	*C*
S(1)	0·028		
S(2)	0·002		
C(3)	−0·011		
N(4)	−0·007*		
C(5)	0·002*		
C(6)	0·004*	−0·017*	−0·032*
C(7)	−0·008*		
C(8)	0·009*		
O(9)	0·089		
N(10)	0·008	0·042*	−0·138*
C(11′)		−0·036*	−0·30
O(12′)		0·016*	−0·19
C(13′)		−0·005*	−0·27
C(11″)		0·25	0·005*
O(12″)		0·41	0·022*
C(13″)		0·32	0·144*

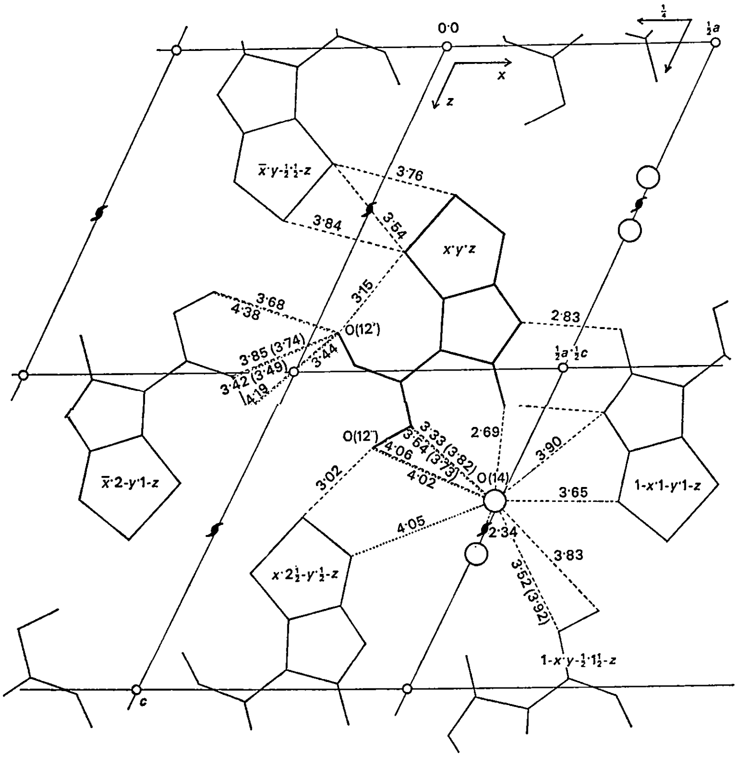

Fig. 4. The structure viewed along the *b* axis. The N–H···O hydrogen bonds are shown together with the surroundings of O(12′), O(12″) and of the water of crystallization [O(14)]. From the molecule (*x*,*y*,*z*) broken lines go to the molecules with the general positions indicated, and dotted lines are drawn to the molecules below. Distances to C(11″) and C(13″) are given in parentheses.

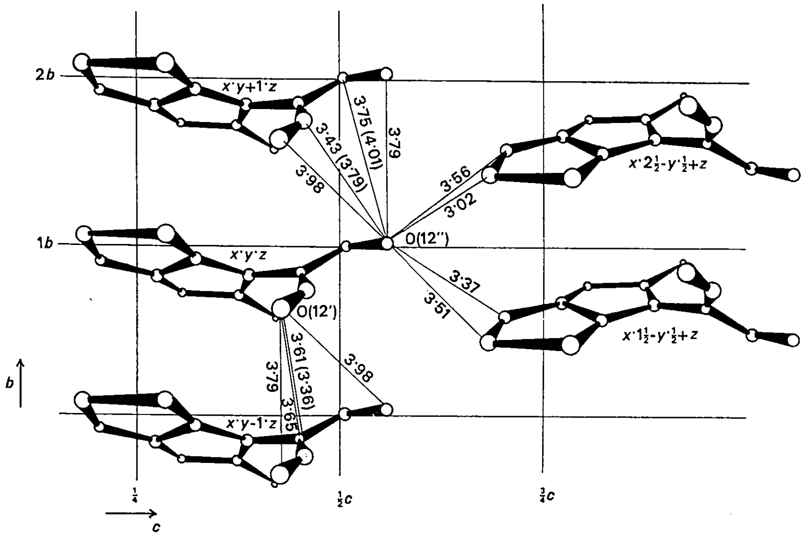

Fig. 5. The structure viewed along the a^* axis. All molecules shown have the same x coordinates. The distances to O(12′) and O(12″) are indicated. Distances to C(11)″ and C(13″) are given in parentheses.

while both of the S–C bond lengths, 1·73 and 1·74 Å, are significantly shorter that the accepted value for a single bond, 1·82 Å (Sutton, 1965), and may be compared with the S–C bonds in thiophen, 1·718 Å (Bak, Christensen, Rastrup-Andersen & Tannenbaum, 1956) and similar compounds. The other bond lengths also show that the π-electrons of the double bonds must be delocalized. The length of N(4)–C(8) is 1·33 Å, a value intermediate between the C–N bond lengths in pyrrole, 1·383 Å (Bak, Christensen, Hansen & Rastrup-Andersen, 1956) and in succinimide, 1·27 Å (Mason, 1956). Finally, the distance N(4)–C(5), 1·37 Å, is similar to the value 1·333 Å given for N–C bonds in amides, (Sutton, 1965).

The angle between the ring plane and the plane of the side chain is about 42° in both of the two molecular conformations. Brown (1966) found a value of 17·6° for the corresponding angle in acetanilide, even though the C(ring)–N–(side chain) bond length of 1·413 Å is of similar length to that of 1·41 Å for the equivalent bond in this molecule.

In one of the two molecular conformations C(11) is the carbonyl carbon atom and C(13) is the methyl carbon atom; in the other the functions of C(11) and C(13) are interchanged. The same two conformations of the vD844 molecules are found also in DMSO-solution (von Daene, Godtfredsen, Tybring & Schaumburg, 1969). As the N–C(=O) bond length is almost certainly shorter than the N–C(H_3) bond length it is unlikely that the individual atoms of the pairs of contributors forming the C(11) and C(13) Fourier peaks respectively should be at exactly the same positions. Therefore two atoms were postulated each for C(11) and C(13). From the final positions of these atoms it seems likely that N(10), C(11′), O(12′) and C(13′) constitute the side chain of one of the molecular conformations of vD844 and N(10), C(11″), O(12″) and C(13″) form the side chain of the other.

Large 'thermal' vibrations are found for O(12′) and O(12″). These could express random variation in the positions of the oxygen atoms which may be induced by the neighbouring molecules having different conformations. Also, large contributions to the 'thermal' parameters may result from the neglect of the three methyl hydrogen atoms, which in one of the molecular conformations are situated close to the positions of the formyl oxygen atoms of molecules in the second conformation. The site occupancies found are 0·64 (e.s.d. 0·04) for both O(12′) and O(12″). The differences from the expected values of 0·5 for each are also probably due to the influence of these methyl hydrogen atoms.

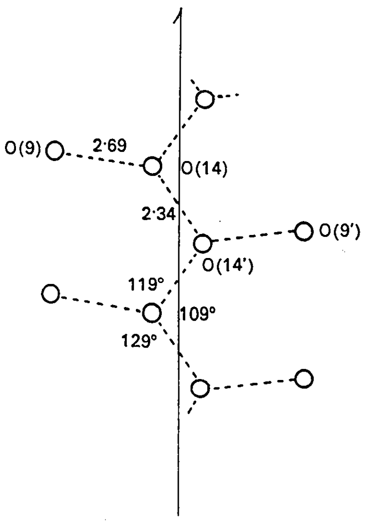

Fig. 6. The hydrogen bond system around the screw axis ($\frac{1}{2},y,\frac{1}{4}$). The system is disordered since only three of every four of the water positions [O(14)] are occupied; the accuracies of the distances and angles shown are low due to variations in the positions of the water molecules.

Table 6. *Observed and calculated structure factors for* vD844

The column headings are the index *l*, $|F_o|$ and $|F_c|$.

0,0,L		
2	166	171
4	657	639
6	137	112
16	152	123
18	143	138
20	129	132
1,0,L		
-22	129	154
-20	161	139
-16	97	96
-14	119	115
-12	84	89
-10	289	263
-8	135	139
-6	315	269
-4	430	360
-2	922	985
0	273	343
2	62	57
4	97	78
6	403	320
8	284	309
10	246	258
12	383	439
14	417	457
16	132	113
2,0,L		
-18	182	160
-16	199	223
-14	364	353
-12	218	244
-10	422	425
-8	925	1040
-4	344	299
-2	482	391
0	852	795
2	119	77
6	84	46
8	199	173
10	528	653
12	350	409
14	168	168
3,0,L		
-20	105	99
-18	214	214
-12	279	297
-10	475	424
-8	385	411
-6	171	137
-4	495	405
-2	452	408
0	659	621
2	929	996
4	615	566
6	140	160
10	294	293
12	132	164
14	166	199
4,0,L		
-22	112	118
-20	97	89
-18	295	290
-16	205	212
-12	306	295
-6	767	797
-4	361	392
-2	424	405
0	382	381
2	779	859
4	480	424
6	335	332
8	229	231
10	180	192
12	420	449
16	241	243
5,0,L		
-20	154	134
-16	218	220
-12	137	136
-10	502	518
-8	448	423
-6	775	760
-4	304	302
-2	752	729
0	388	280
2	594	544
4	187	189
6	193	211
8	89	67
10	171	191
12	166	154
14	258	261
16	152	168
6,0,L		
-12	308	305
-10	195	195
-8	900	951
-6	322	319
-4	321	309
-2	535	493
0	482	491
2	494	470
4	581	610
6	218	236
8	135	96
12	210	198
14	185	186
16	115	114
7,0,L		
-16	108	106
-14	137	124
-12	101	109
-10	372	393
-4	112	99
-2	125	126
0	152	124
2	549	638
4	337	362
6	458	543
12	171	157
8,0,L		
-16	242	327
-14	155	149
-12	176	224
-10	115	91
-8	168	141
-6	252	263
-4	79	59
-2	84	54
0	289	265
2	258	271
4	352	415
8	146	114
10	146	173
12	119	116
14	129	141
9,0,L		
-14	115	126
-10	132	153
-8	187	178
-6	279	331
-4	434	475
-2	173	160
0	79	58
4	132	125
6	321	334
12	129	137
10,0,L		
-16	210	206
-14	123	120
-12	101	100
-10	203	231
-6	562	600
-4	79	60
-2	123	106
0	105	112
4	339	388
6	137	135
8	238	225
12	79	90
11,0,L		
-18	132	143
-12	229	268
-10	270	294
-6	146	141
-4	146	148
-2	219	242
2	252	261
4	152	136
6	312	291
8	190	192
12,0,L		
-14	222	209
-12	159	152
-10	219	223
-8	188	155
-6	241	253
-4	341	371
-2	164	163
0	125	98
4	236	218
6	135	120
13,0,L		
-6	308	303
-4	108	82
-2	156	154
14,0,L		
-12	156	142
-8	137	131
15,0,L		
-16	129	117
-12	132	121
0	149	167
16,0,L		
-14	145	135
-4	140	141
-2	182	173
0	79	80
17,0,L		
-10	112	97
-6	93	91
-4	89	105
-2	62	83
0,1,L		
5	72	89
6	41	33
7	492	502
8	178	156
9	91	100
10	208	257
11	348	447
12	148	153
13	307	351
14	83	75
17	116	104
21	58	62
1,1,L		
-17	102	101
-16	77	77
-15	165	168
-14	149	136
-13	138	141
-12	229	245
-11	235	271
-10	156	222
-9	270	266
-7	66	64
-6	191	202
-5	46	51
-4	329	376
-3	300	300
-2	457	703
-1	298	379
0	494	734
1	809	1036
2	738	904
3	593	664
4	46	30
5	342	325
6	116	72
8	190	151
9	244	250
10	62	32
11	144	158
13	109	130
14	135	131
15	46	25
19	88	79
2,1,L		
-21	151	138
-20	93	58
-19	150	146
-17	143	127
-16	128	120
-13	163	167
-12	104	104
-11	182	160
-9	106	108
-8	227	241
-7	173	181
-6	120	140
-5	239	226
-4	136	113
-3	473	575
-1	988	1373
0	539	722
1	93	76
2	495	554
3	458	548
4	153	152
5	116	122
6	104	67
8	77	72
9	169	178
10	138	127
12	125	107
13	317	323
15	153	138
16	150	143
3,1,L		
-21	106	96
-20	121	97
-19	128	104
-18	125	114
-16	235	214
-14	178	178
-13	62	65
-12	151	150
-11	175	175
-10	143	142
-9	328	362
-8	50	64
-7	524	594
-6	95	108
-5	196	227
-4	183	191
-3	237	231
-2	639	763
-1	385	493
0	46	44
1	301	275
2	171	133
3	181	143
4	66	47
5	116	112
6	321	313
7	83	69
8	189	176
9	156	163
11	385	434
13	283	302
14	238	254
15	226	200
4,1,L		
-21	108	92
-18	112	106
-17	114	101
-16	69	64
-15	104	96
-14	91	91
-13	62	62
-12	112	103
-11	401	437
-10	143	128
-9	397	374
-8	351	334
-7	378	378
-6	88	86
-5	246	261
-4	199	207
-3	320	304
-1	339	351
0	55	39
1	280	243
2	243	201
3	156	154
4	259	257
5	475	508
7	149	128
8	91	97
9	239	299
11	155	154
12	167	170
13	164	184
14	150	141
5,1,L		
-21	116	113
-19	88	64
-17	95	89
-16	121	109
-14	130	122
-13	114	104
-12	80	76
-11	234	227
-10	399	455
-9	397	442
-8	229	234
-7	161	152
-6	215	191
-5	75	71
-4	22	37
-1	110	117
0	350	343
1	415	421
2	205	192
3	496	556
4	198	241
5	272	286
6	160	136
7	234	249
9	125	102
10	192	97
12	194	119
14	93	107
17	66	68
6,1,L		
-21	69	73
-20	46	44
-19	191	188
-18	93	104
-15	193	168
-14	62	55
-13	83	88
-12	164	169
-11	83	80
-9	121	143
-8	140	135
-7	319	358
-6	55	40
-5	227	218
-3	215	245
-2	125	156
-1	252	267
0	257	296
1	488	555
3	405	423
4	222	233
5	312	370
7	91	69
8	46	58
9	172	169
12	182	160
13	69	54
14	85	74
15	173	179
16	114	101
7,1,L		
-20	108	95
-19	106	91
-17	177	188
-11	165	174
-10	179	178
-9	182	177
-8	110	117
-7	372	391
-6	136	116
-5	165	174
-4	372	426
-2	278	307
0	83	57
1	257	269
2	200	222
5	85	75
6	88	60
7	161	149
8	106	104
13	177	179
14	118	115
15	167	198
8,1,L		
-16	116	121
-15	114	108
-14	102	91
-13	126	107
-12	130	115
-9	418	525
-8	258	296
-6	164	162
-5	335	328
-3	160	177
-2	66	64
-1	75	64
1	190	178
2	41	45
3	169	188
4	308	335
5	289	323
7	204	213
8	181	187
13	177	178
9,1,L		
-19	97	83
-18	88	82
-17	159	164
-15	135	146
-12	77	87
-10	177	206
-9	91	98
-8	116	117
-7	144	156
-6	138	144
-2	123	138
-1	118	100
1	118	137
2	276	267
3	302	335
5	274	288
6	261	280
7	148	155
9	110	90
10,1,L		
-19	91	80
-17	204	201
-14	114	128
-12	100	104
-11	97	81
-9	118	126
-6	177	202
-5	144	152
-3	284	340
-1	110	124
0	108	84
1	178	193
2	55	47
3	116	100
4	125	115
5	171	153
6	106	102
7	102	78
8	100	75
11,1,L		
-16	104	103
-14	164	167
-12	121	113
-10	120	112
-9	45	62
-8	241	250
-7	202	228
-5	353	392
-4	118	127
-3	185	158
2	95	86
3	77	76
5	118	88
6	112	102
8	85	99
9	138	133
12,1,L		
-17	91	83
-14	114	99
-12	102	89
-11	91	81
-10	91	61
-8	178	204
-7	231	269
-5	108	82
-4	133	120
-1	97	78
2	95	101
3	80	76
4	185	167
5	85	82
6	83	73
7	235	240
8	69	69
13,1,L		
-16	95	75
-15	114	107
-14	50	47
-13	136	137
-12	91	90
-10	121	107
-7	91	85
-5	102	97
-3	83	81
-2	77	82
0	120	124
3	100	79
5	157	165
6	66	70
14,1,L		
-13	85	68
-9	135	85
-7	128	106
-5	100	107
-4	210	184
-3	97	96
-2	72	65
-1	159	139
15,1,L		
-6	157	133
-5	95	98
-4	66	46
-3	156	150
-1	85	69
0,2,L		
1	189	204
2	514	575
3	382	400
4	126	93
5	97	74
6	160	183
7	147	135
8	61	56
11	173	153
13	281	277
14	135	124
15	80	72
17	76	72
18	89	92
19	65	58
1,2,L		
-20	86	92
-19	80	75
-18	100	97
-17	86	95
-14	92	63
-11	142	137
-10	135	164
-9	319	336
-8	122	120
-7	138	123
-6	100	72
-5	51	55
-4	189	176
-3	168	160
-2	73	38
-1	252	286
0	251	241
1	528	545
2	299	306
4	177	186
5	161	155
6	100	59
7	185	190
8	83	91
9	250	263
10	136	161
11	299	320
12	254	232
13	86	69
14	113	89
15	242	209
2,2,L		
-20	73	76
-13	235	220
-12	140	151
-11	271	314
-10	183	200
-9	259	259
-8	260	244
-7	126	127
-6	195	210
-5	97	104
-4	61	40
-2	169	183
-1	120	108
0	128	97
1	238	227
2	264	236
3	467	454
4	177	164
5	251	256
6	169	132
7	126	116
8	97	88
9	150	154
10	264	300
11	103	101
12	138	119
13	157	167
14	100	82
15	73	67
3,2,L		
-20	100	108
-14	86	64
-13	208	217
-12	151	150
-11	128	110
-10	122	91
-9	262	307
-8	165	163
-7	65	73
-6	193	243
-5	135	177
-4	100	75
-3	177	182
-2	95	77
-1	192	209
0	332	426
1	704	792
2	179	190
3	328	331
4	311	306
5	264	250
7	65	53
11	86	81
12	73	91
17	73	84
4,2,L		
-21	76	80
-20	89	87
-19	65	83
-16	140	117
-15	86	76
-14	124	122
-13	92	85
-12	136	154
-11	140	137
-10	208	226
-9	80	82
-8	95	106
-6	173	198
-5	151	131
-4	57	56
-3	122	129
-2	234	242
-1	415	454
0	73	80
1	447	495
2	366	344
3	169	159
4	205	176
5	161	144
6	122	88
7	65	40
10	97	97
11	103	102
12	83	71
13	150	133
14	136	149
15	193	197
5,2,L		
-21	57	61
-19	95	71
-18	80	86
-17	171	151
-15	189	175
-14	86	100
-13	83	52
-11	86	64
-10	158	156
-9	165	196
-8	321	369
-7	264	299
-6	160	132
-5	65	49
-4	171	136
-3	57	46
-2	76	66
-1	216	188
0	144	125
1	83	80
2	128	114
3	76	75
4	110	102
5	151	151
9	154	161
10	80	81
11	200	207
12	177	174
13	242	235
14	95	113
15	161	170
6,2,L		
-21	51	60
-15	108	89
-11	193	236
-10	183	205
-9	247	270
-8	176	185
-7	142	160
-6	73	69
-5	189	224
-4	182	221
0	57	9
1	120	88
2	86	61
3	83	58
4	193	200
5	300	320
6	176	160
7	135	122
10	83	94
11	176	154
12	69	44
13	133	141
14	80	70
7,2,L		
-21	61	56
-17	153	178
-16	128	131
-15	86	71
-14	73	62
-13	80	76
-11	163	152
-9	86	102
-7	269	307
-6	118	117
-5	136	128
0	147	145
1	92	81
2	65	65
3	361	427
4	341	369
5	124	115
6	126	111
7	199	204
13	80	86
8,2,L		
-19	126	135
-16	196	182
-12	106	99
-11	69	68
-9	83	69
-8	92	82
-7	83	60
-6	83	82
-5	231	263
-4	138	133
-3	209	260
-1	133	150
1	192	177
3	258	242
5	158	158
6	118	97
12	65	25
9,2,L		
-21	61	79
-15	124	124
-14	73	85
-13	106	106
-11	150	159
-8	144	149
-7	344	380
-6	118	138
-5	202	219
-4	216	199
-2	144	127
-1	83	68
0	83	66
1	108	81
3	92	78
7	118	115
8	92	99
9	86	88
10,2,L		
-14	144	170
-9	192	221
-7	185	201
-6	173	147
-4	160	152
3	106	100
5	138	136
6	126	132
7	249	273
8	92	93
11,2,L		
-15	150	157
-14	110	112
-10	73	62
-9	95	113
-8	108	116
-2	126	85
3	174	154
4	165	149
5	238	241
6	113	117
7	73	79
12,2,L		
-12	142	138
-7	140	138
-4	153	156
-3	161	182
-1	126	121
0	146	123
2	76	66
3	83	74
4	65	46
5	120	134
13,2,L		
-9	97	78
-8	83	74
-5	207	224
-4	161	136
-3	154	153
-2	100	96
3	76	80
14,2,L		
-9	108	99
-7	76	57
-6	76	74
-5	110	141
1	73	75
15,2,L		
-3	83	94
-1	65	86
16,2,L		
-5	83	105

Table 6 (*cont.*)

0,3,L		
2	167	113
5	156	157
6	127	114
8	222	245
9	82	80
10	279	296
11	112	146
12	156	149
14	77	83
1,3,L		
−14	82	62
−12	321	343
−10	167	164
−8	127	130
−5	127	132
−4	116	106
−2	200	138
0	324	208
1	119	80
2	276	180
3	143	148
4	361	336
6	71	49
7	77	68
8	127	118
9	92	82
2,3,L		
−14	151	141
−11	101	115
−10	77	81
−9	77	72
−8	148	147
−7	71	73
−6	101	100
−5	112	93
−4	77	69
−3	87	66
−2	175	145
0	429	315
1	208	205
2	507	500
4	162	150
5	105	88
10	87	73
14	101	106
3,3,L		
−10	224	242
−8	154	164
−7	92	86
−6	172	154
−5	112	106
−4	108	111
−2	169	120
0	389	359
1	156	129
2	143	114
3	133	139
5	123	98
6	133	129
8	112	90
9	101	108
12	177	185
14	151	168
14	151	168
15	58	21
4,3,L		
−12	112	110
−10	222	268
−9	101	115
−8	177	188
−7	143	128
−6	101	108
−3	112	123
−2	123	101
0	101	90
1	165	180
2	321	337
3	140	124
4	148	120
6	175	163
7	77	69
10	123	126
11	77	85
12	159	142
14	96	131
5,3,L		
−18	65	79
−16	87	78
−15	154	158
−12	177	199
−10	127	107
−8	96	93
−6	140	147
−5	77	75
−1	105	115
0	304	328
2	190	176
4	341	360
5	119	94
12	101	94
6,3,L		
−18	101	115
−17	105	114
−16	105	102
−14	112	122
−13	87	92
−6	159	195
−4	82	64
−1	92	78
0	136	137
1	87	.89
2	202	254
3	189	210
4	136	113
6	96	71
7	92	87
12	82	95
7,3,L		
−16	108	94
−14	112	118
−10	130	143
−8	148	181
−6	214	272
−5	119	125
−4	156	163
−3	82	90
−1	71	70
0	165	185
4	87	74
8	96	99
8,3,L		
−13	123	128
−10	119	129
−9	112	110
−8	167	195
−7	92	89
−6	203	243
−5	77	88
−3	77	67
4	130	129
6	197	194
8	96	118
9,3,L		
−14	101	83
−13	108	99
−11	87	82
−10	87	77
−8	116	137
−7	77	75
−3	101	50
−1	96	61
1	87	29
4	222	258
6	200	205
10,3,L		
−16	87	86
−15	101	98
−6	169	181
−4	96	119
2	186	212
4	119	110
11,3,L		
−4	116	107
−3	92	69
−2	127	137
−1	96	105
0	71	66

The position of O(14), the oxygen atom in the water molecule, is not well defined. Its 'vibrational' parameters shown diagrammatically in Fig. 3, are extremely large. The multiplicity found for O(14) is only 0·80, possibly because the close packing around the water molecules leaves sufficient space for only about three of any four equivalent positions to be occupied. One water molecule may cause those immediately above and below it to move a little upwards/sideways and downwards/sideways respectively, and these displacements may not leave enough space for the next molecules in the series to occupy their expected 'ordered' positions. Eventually, the displacements become such that one 'ordered' position is omitted.

The water molecules are involved in a disordered hydrogen bond system. Each water molecule can act as donor for two hydrogen bonds, one to a carbonyl oxygen atom, O(9), and one to a neighbouring water molecule; and it accepts a hydrogen bond from another water molecule, see Fig. 6. The O(9)---O(14) distance is about 2·69 Å and it is nearly unaffected by the possible variable position of O(14) since the direction of the greatest 'vibration' for this atom is roughly perpendicular to the O(9)–O(14) direction. The average distance between the oxygen atoms in neighbouring water molecules is 2·34 Å. The length of the centred hydrogen bond in potassium hydrogen chloromaleate is 2·40 Å (Ellison & Levy, 1965), so this length is much too short, even for an O–H---O hydrogen bond. The vD844 molecules themselves are connected in pairs by hydrogen bonds, N(4)---O(9), of length 2·83 Å. The deviation of O(9) from the ring plane *A* is 0·09 Å in the direction of the neighbouring N(4) atom.

The surroundings of O(12′) and O(12″) are illustrated in Figs. 4 and 5. Since no really close contacts to side chains in other molecules exist, order in the distribution of the two molecular conformations is probably very unlikely, even around a single row of symmetry centres, *e.g.* $(0,n\times\frac{1}{2},\frac{1}{2})$; and, further, it is even more unlikely that some possible order could be translated to the next, equivalent row of symmetry centres, *e.g.* $(1,n\times\frac{1}{2},\frac{1}{2})$.

The disulfide groups are arranged closely around the screw axes. S---S contacts between disulfide groups have been found in several crystal structures, (Fridrichsons & Mathieson, 1967), and they may exercise a strong influence on the molecular packing. Further close sulphur contacts are an intramolecular distance of 3·15 Å between S(1) and O(12′) and an intermolecular distance of 3·02 Å between S(2) and O(12″). The sum of the van der Waals radii is 3·25 Å [= 1·85 + 1·40, Pauling (1960)], so these distances may indicate weak oxygen–sulphur attractions.

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