such interactions have been minimized by taking a boat form.

Thus, there is a gradual change in the detailed geometry throughout the molecules of the series in the crystalline state. This change in geometry parallels that of chemical properties.

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The Crystal and Molecular Structure of 3-Carboxymethylthio-1,5-diphenylformazan

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Abstract

$C_{15}H_{14}N_4O_2S$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 27{\cdot}98$ (1), $b = 10{\cdot}127$ (5), $c = 5{\cdot}208$ (3) Å, $\beta = 91{\cdot}59$ (5)°, $Z = 4$. The structure was refined to $R = 0{\cdot}053$ for 965 observed reflections. The molecules are remarkably planar and are strongly hydrogen bonded through their carboxylic groups to form dimers (O···O = 2·66 Å). The imino proton participates in a weak intramolecular hydrogen bond which stabilizes the N—N—C—N—N chain in a *syn,s-trans* configuration relative to the formal double C=N and single C—N bonds.

Introduction

3-Carboxymethylthio-1,5-diphenylformazan (3) is being studied as a potential terdentate ligand since it incorporates the chromophoric groups of dithizone (1) (Irving, 1977) and *S*-methyldithizone (2) (Irving, Nabilsi & Sahota, 1973), and unlike the latter contains an acidic group which should facilitate the formation of metal chelates and lend itself to liquid–liquid extraction procedures. However, complete absence of the expected metal complexes, coupled with exceptional acid dissociation constants, unusual visible, IR and NMR spectroscopic properties and the existence of (3) as a monomer in solution, suggested a conformation in which the —OH group of the side chain points almost axially through the centre of the π-electron system of a quasi-aromatic formazan ring, as (5) (Hutton, Irving, Koch, Nassimbeni & Gafner, 1979). Although hydrogen bonding to π-electron systems is well established (Joesten & Schaad, 1974), there are few precedents for the novel structure (5) and an X-ray crystallographic investigation of (3) was undertaken to ascertain whether this molecular structure persisted in the solid state.

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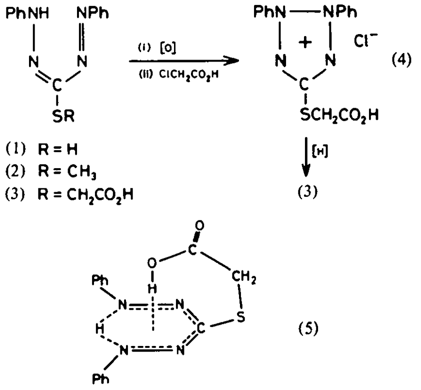

The only previous crystal structure determination of an *S*-alkylated formazan is that of (2) (Preuss & Gieren, 1975), which is almost planar and has a *syn,s-trans* configuration relative to the formal double C=N and single C—N bonds, this configuration being effectively stabilized by the participation of the imino proton in a weak intramolecular hydrogen bond. The crystal structure of the parent compound (1) has recently been refined (Laing, 1977).

Experimental

Preparation

(3) was prepared by reduction of tetrazolium chloride (4) (Ogilvie & Corwin, 1961) and purified by recrystallization from an ethanol–water mixture. Crystals were grown by allowing *n*-hexane vapour to diffuse slowly into a benzene solution of (3). The fragile needles (m.p. 421–422 K, dec.) were elongated along **c** and had a bronze reflex. (Composition: found: C 57·3, H 4·45, N 17·7%; calculated for $C_{15}H_{14}N_4O_2S$: C 57·3, H 4·5, N 17·8%.)

Crystal and intensity data

$C_{15}H_{14}N_4O_2S$, M_r = 314·36, monoclinic, a = 27·98 (1), b = 10·127 (5), c = 5·208 (3) Å, β = 91·59 (5)°, V = 1475·34 Å^3, D_m = 1·39 (by flotation in aqueous KI), Z = 4, D_c = 1·42 Mg m^{-3}, $F(000)$ = 656; Mo $K\alpha$ radiation, λ = 0·7107 Å; μ(Mo $K\alpha$) = 0·184 mm^{-1}. The systematic extinctions $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$ indicated the space group $P2_1/n$.

Preliminary cell dimensions and space-group symmetry were determined from photographs. Considerable difficulty was encountered in the selection of a suitable crystal for data collection because most specimens were twinned. Laing (1977) has remarked on the susceptibility of (1) to twinning. Eventually a single crystal 0·1 × 0·1 × 0·5 mm was found and accurate cell dimensions were obtained by least squares from the settings of 25 high-order reflections measured on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Intensities were collected by the ω–2θ scan technique [scan width 0·5° (θ), scan speed 0·01° (θ) s^{-1}] in the range $3 \le \theta \le 20$°. The intensities of three reference reflections monitored after every 68 measured reflections remained constant to within ±1% of their mean values. 1457 reflections were collected; with the criterion $I_{\rm rel} > 2\sigma(I_{\rm rel})$ for an observed reflection and omitting systematic absences, 965 unique reflections remained which were employed in the analysis. Lorentz–polarization corrections were applied but no correction was made for absorption.

Structure determination and refinement

The structure was solved by the automatic centrosymmetric routine of *SHELX* (Sheldrick, 1976), in which an E map yielded the positions of all the heavy atoms. The final full-matrix least-squares refinement was carried out with the S atom treated anisotropically and the remaining non-hydrogen atoms isotropically. The H atoms, all of which had been revealed in difference Fourier maps, were subjected to constrained refinement. Those bonded to C were constrained to ride at 1·08 Å from their corresponding parent atoms, their positions being dictated by the geometry of the

Table 1. *Fractional coordinates* (×10^4) *and isotropic thermal motion parameters* (Å^2 ×10^3) *of the non-hydrogen atoms, with e.s.d.'s in parentheses*

	x	y	z	$U_{\rm iso}$
C(11)	2298 (2)	−4 (6)	1193 (10)	47 (2)
C(12)	2318 (2)	953 (6)	−734 (10)	50 (2)
C(13)	2698 (2)	897 (6)	−2409 (10)	58 (2)
C(14)	3043 (2)	−70 (6)	−2207 (11)	61 (2)
C(15)	3013 (2)	−1011 (6)	−320 (10)	58 (2)
C(16)	2640 (2)	−996 (6)	1396 (10)	54 (2)
C(51)	910 (2)	−1345 (5)	9527 (9)	47 (2)
C(52)	507 (2)	−1497 (6)	11024 (10)	58 (2)
C(53)	504 (2)	−2445 (6)	12946 (10)	60 (2)
C(54)	897 (2)	−3226 (6)	13417 (10)	60 (2)
C(55)	1302 (2)	−3084 (6)	11935 (10)	59 (2)
C(56)	1306 (2)	−2150 (5)	9991 (10)	51 (2)
C(3)	1226 (2)	722 (5)	4392 (10)	46 (2)
C(7)	869 (2)	2725 (6)	1483 (10)	54 (2)
C(8)	489 (2)	3727 (6)	925 (10)	54 (2)
N(1)	1935 (2)	−18 (5)	2981 (9)	56 (1)
N(2)	1572 (1)	859 (5)	2762 (7)	48 (1)
N(4)	1251 (1)	−296 (4)	6232 (8)	50 (1)
N(5)	889 (2)	−328 (4)	7659 (8)	51 (1)
O(81)	141 (1)	3889 (4)	2242 (7)	64 (1)
O(82)	567 (1)	4418 (4)	−1191 (8)	66 (1)
S(6)	725 (1)	1769 (2)	4272 (3)	†

† Anisotropic thermal parameters are in the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots) \times 10^3]$ with parameters: U_{11} = 67 (1), U_{22} = 67 (1), U_{33} = 51 (1), U_{12} = 16 (1), U_{13} = 11 (1) and U_{23} = 9 (1).

Table 2. *Fractional coordinates* ($\times 10^3$) *of the hydrogen atoms*

	x	y	z		x	y	z
H(12)	205	171	−92	H(54)	89	−395	1493
H(13)	272	163	−390	H(55)	161	−370	1230
H(14)	334	−9	−352	H(56)	162	−205	883
H(15)	328	−178	−17	H(71)	90	207	−15
H(16)	262	−174	287	H(72)	121	322	183
H(52)	20	−88	1068	H(N1)	189	−76	423
H(53)	19	−257	1408	H(O2)	31	509	−117

molecule. Their isotropic temperature factors were treated as two single parameters which refined to $U = 0{\cdot}094$ (6) (aromatic H) and 0·064 (11) Å^2 (methylene H). H(N1) and H(O2) were fixed at 1·00 Å from N(1) and O(82) and their temperature factors were refined independently to $U = 0{\cdot}16$ (3) and 0·22 (4) Å^2 respectively. The refinement converged to $R = 0{\cdot}053$, while $R_w = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o| = 0{\cdot}050$ with the weighting scheme $w = 1/(\sigma^2 F_o + gF_o^2)$. The final value of g (0·000096) was chosen to give the smallest systematic variation of $w\Delta^2$ with the magnitude of F_o, as shown by an analysis of variance computed after the final cycle.* In the final cycle the mean e.s.d. in the parameters of the non-hydrogen atoms was >100 times the average parameter shift. A final difference map showed no peaks >0·2 e Å^{-3}. Tables 1 and 2 list the final atomic positions and thermal parameters.

All computations were performed at the Computer Centre of the University of Cape Town on a Univac 1106 computer with *SHELX* (data reduction, structure solution and refinement), *XANADU* (molecular geometry) and *PLUTO* (illustrations) (Sheldrick, 1976; Roberts & Sheldrick, 1975; Motherwell, 1975).

Results and discussion

Molecular structure

The molecular structure and atomic nomenclature are shown in Fig. 1. The molecules are remarkably planar and are strongly hydrogen bonded through their carboxylic groups to form dimers. The imino proton H(N1) is internally hydrogen bonded to N(4), effectively locking the molecule in a *syn,s-trans* configuration with an intramolecular hydrogen bridge forming a five-membered ring. This configuration of the N–N–C–N–N chain is the same as in (2) (Preuss & Gieren, 1975). Fig. 2 depicts the dimer and gives interatomic distances and angles.

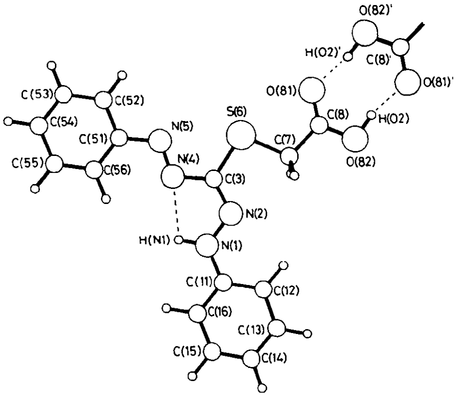

Fig. 1. The molecular structure, showing a portion of the symmetry-related moiety of the dimer and the atomic nomenclature. H atoms are numbered according to the atom to which they are bonded. The dashed lines indicate hydrogen bonds. The symmetry code for the superscript is given in Table 5.

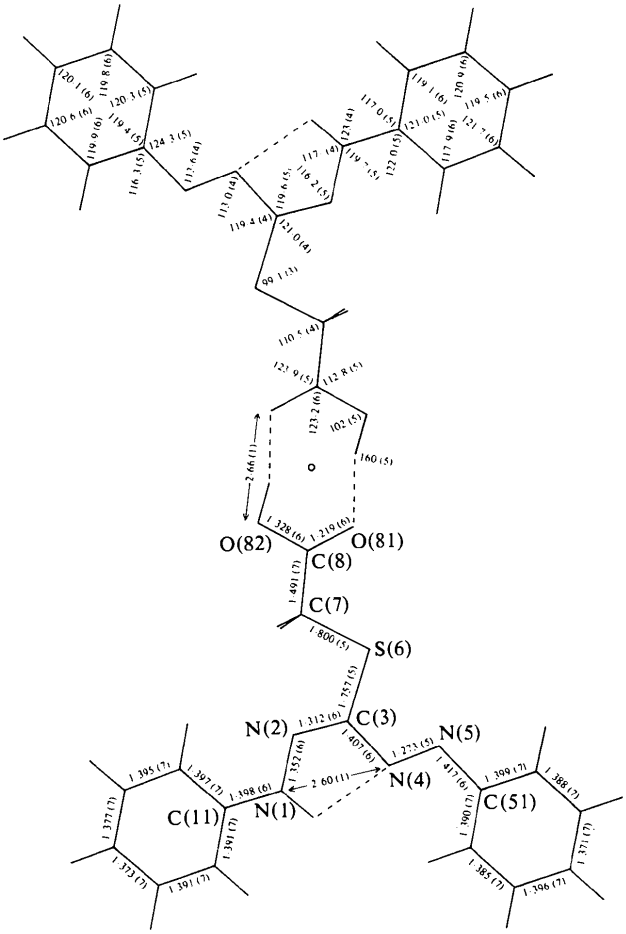

Fig. 2. The dimer, showing interatomic distances (Å; lower molecule) and angles (°; upper molecule). The dashed lines indicate hydrogen bonds. The two molecules comprising the dimer are related by a centre of inversion.

* The analysis of variance and a list of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34209 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Torsion angles* (°)

The torsion angle $\omega(I-J-K-L)$ is defined as the angle between the vector $J-I$ and the vector $K-L$ when viewed down $J-K$. The sign of ω is positive if $J-I$ is to be rotated clockwise into $K-L$ and negative if counterclockwise (Klyne & Prelog, 1960). Phenyl-ring torsion angles are all <1·5° and are omitted. E.s.d.'s are *ca* 0·5°.

N(1)–C(11)–C(12)–C(13)	179·1	C(52)–C(51)–N(5)–N(4)	−175·2	S(6)–C(7)–C(8)–O(81)	2·2
N(1)–C(11)–C(16)–C(15)	−179·1	C(56)–C(51)–N(5)–N(4)	6·8	S(6)–C(7)–C(8)–O(82)	−177·0
C(12)–C(11)–N(1)–N(2)	4·5	N(4)–C(3)–N(2)–N(1)	0·0	C(8)–C(7)–S(6)–C(3)	180·0
C(12)–C(11)–N(1)–H(N1)	172·3	S(6)–C(3)–N(2)–N(1)	−178·5	C(7)–C(8)–O(82)–H(O2)	−173·9
C(16)–C(11)–N(1)–N(2)	−174·9	N(2)–C(3)–N(4)–N(5)	−178·9	O(81)–C(8)–O(82)–H(O2)	7·0
C(16)–C(11)–N(1)–H(N1)	−7·1	S(6)–C(3)–N(4)–N(5)	0·0	C(11)–N(1)–N(2)–C(3)	175·0
N(5)–C(51)–C(52)–C(53)	−178·1	N(2)–C(3)–S(6)–C(7)	3·4	H(N1)–N(1)–N(2)–C(3)	6·6
N(5)–C(51)–C(56)–C(55)	177·2	N(4)–C(3)–S(6)–C(7)	−175·4	C(3)–N(4)–N(5)–C(51)	180·0

The calculated bond lengths (Fig. 2) reveal a marked delocalization of π electrons within the N–N–C–N–N chain and with the phenyl rings. While the formal double bonds C(3)=N(2) (1·31 Å) and N(4)=N(5) (1·27 Å) are clearly extended in comparison with isolated double bonds, the formal single bonds C(3)–N(4) (1·41 Å) and N(1)–N(2) (1·35 Å) are noticeably shortened. The S–C lengths are of the expected magnitude and show that the electron delocalization found in the N–N–C–N–N chain does not extend to the thioacetic acid portion of the molecule. In dimethyl sulphide, CH_3SCH_3, C–S = 1·802 (2) Å and C–S–C = 98° 52 (10)′ (Pierce & Hayashi, 1961). The C(3)–S(6)–C(7) angle of 99·1° in (3) is therefore normal and the difference between S(6)–C(3) (1·76 Å) and S(6)–C(7) (1·80 Å) follows from the difference in hybridization of the two C atoms [C(3) sp^2, C(7) sp^3]. The C(7)–C(8) distance (1·49 Å), while significantly shortened from the standard single-bond value of 1·54 Å, is the same as the corresponding distance found in the benzoic acid dimer (Sim, Robertson & Goodwin, 1955), while the C(8)=O(81) (1·22 Å) and C(8)–O(82) (1·33 Å) lengths correspond favourably with the representative distances C=O (1·23 Å) and C–OH (1·31 Å) given by Dunitz & Strickler (1968) for a typical carboxylic acid dimer. The synplanar arrangement S(6)–C(7)–C(8)=O(81) is a general feature of the molecular shapes of saturated carboxylic acids and the torsion angle ω is usually found to be <10° (Dunitz & Strickler, 1968); in (3), ω(S–C–C=O) is 2·2° (Table 3). Bond distances and angles relating to the phenyl groups are generally satisfactory; the mean C–C distance in the two phenyl rings is 1·388 (9) Å.

The parameters for some least-squares planes are listed in Table 4, where the deviations of atoms from the planes they define illustrate the expected planarity of the N–N–C–N–N chain consequent on electron delocalization. The largest deviation from the N–N–C(S)–N–N plane (plane 3) is 0·01 Å. Planarity, however, extends to the whole molecule at x,y,z (plane 2) and further to include the symmetry-related moiety of the dimer at $-x$, $1-y$, $-z$ (plane 1). Thus the largest deviation from the least-squares plane calculated through all the non-hydrogen atoms of the dimer (plane 1) is only 0·19 Å. The coplanarity of the thioacetic acid chain with the N–N–C–N–N chain does not have an explanation in electronic terms, since electron delocalization has been shown above not to extend beyond the Ph–N–N–C–N–N–Ph chain. It seems likely, therefore, that the extraordinary planarity of the dimer is a result of electron delocalization in the N–N–C–N–N chain and dimer formation between the thioacetic acid chains, as well as molecular-packing considerations. The torsion angles listed in Table 3 emphasize the remarkable planarity of (3); there is no torsion angle between non-hydrogen-atom sequences whose absolute value is >6·8°.

The phenyl rings are twisted slightly out of the mean plane of the molecule in opposite senses, the angle between the normals to each phenyl-ring plane being 11·8°. Thus, C(15) and C(16) of ring 1 are below the plane by 0·14 and 0·09 Å, respectively, while it is C(52) and C(53) of ring 5 which each lie 0·18 Å below the plane. The difference in exterior angles at C(11) and C(51) [117·0 and 122·0° at C(11); 116·3 and 124·3° at C(51)] is the same as that in (2) (Preuss & Gieren, 1975) and is explained by the steric interaction of the phenyl rings with atoms in the N–N–C–N–N chain. It can be seen (non-bonded distances are given in Table 5) that the intramolecular contact distance C(56)···N(4) (2·71 Å) is shorter than C(12)···N(2) (2·81 Å) and thus the steric effect should be larger for the former contact. The angles at C(11) and C(51) show that this is indeed the case. The near coplanarity of both phenyl rings with the N–N–C–N–N chain confirms that the imino proton H(N1) is bonded to N(1) because a H atom attached to either N(2) or N(4) would necessarily interfere with H(12) or H(56) on phenyl rings 1 and 5, respectively, and force the phenyl ring out of the plane of the molecule.

Hydrogen bonding

Inter- and intramolecular hydrogen-bond data are given in Table 5 and hydrogen bonds are shown as dashed lines in the molecular illustrations. Molecules of

Table 4. *Least-squares planes*

(*a*) Equations of least-squares planes expressed in orthogonalized space as $PI + QJ + RK = S$

Plane 1: all non-hydrogen atoms of the dimer, *i.e.* of the molecules at x,y,z and $-x, 1-y, -z$:

$$12{\cdot}746I + 6{\cdot}544J + 3{\cdot}122K = 3{\cdot}272.$$

Plane 2: all non-hydrogen atoms of one molecule at x,y,z:

$$13{\cdot}115I + 6{\cdot}407J + 3{\cdot}142K = 3{\cdot}348.$$

Plane 3: C(3), N(1), N(2), N(4), N(5), S(6):

$$12{\cdot}720I + 6{\cdot}270J + 3{\cdot}268K = 3{\cdot}435.$$

Plane 4: phenyl ring (1): C(11)–C(16):

$$14{\cdot}816I + 5{\cdot}884J + 3{\cdot}142K = 3{\cdot}769.$$

Plane 5: phenyl ring (5): C(51)–C(56):

$$9{\cdot}794I + 6{\cdot}828J + 3{\cdot}335K = 3{\cdot}148.$$

(*b*) Deviations (Å $\times 10^3$) from planes. Atoms not included in the calculation are marked by asterisks. All e.s.d.'s are <0·008 Å.

	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5
C(11)	27	38	−124*	8	−502*
C(12)	76	71	−129*	−5	−472*
C(13)	2	8	−228*	−1	−697*
C(14)	−129	−96	−330*	4	−952*
C(15)	−194	−145	−341*	−1	−994*
C(16)	−123	−85	−245*	−5	−777*
C(51)	−18	−23	−7*	−219*	2
C(52)	−164	−179	−126*	−436*	3
C(53)	−187	−186	−96*	−394*	−6
C(54)	−50	−22	69*	−123*	3
C(55)	96	134	189*	95*	2
C(56)	104	126	143*	39*	−5*
C(3)	134	101	12	−149*	10*
C(7)	82	3	−136*	−412*	59*
C(8)	80	−28	−173*	−560*	185*
N(1)	113	114	−11	23*	−271*
N(2)	155	131	5	−68*	−101*
N(4)	75	61	8	−132*	−46*
N(5)	38	14	−6	−239*	53*
O(81)	153	33	−84*	−567*	394*
O(82)	−30	−148	−333*	−704*	27*
S(6)	144	79	−7	−312*	195*

(*c*) Selected angles (°) between normals to planes. All e.s.d.'s are <0·8°.

Planes 1 and 2	1·1	Planes 3 and 4	5·0
Planes 2 and 3	1·8	Planes 3 and 5	6·8
Planes 2 and 4	4·6	Planes 4 and 5	11·8
Planes 2 and 5	7·5		

The angle between the normal to plane 2 and the C(3)–S(6) vector is 90·7°.

Table 5. *Intra- and intermolecular distances* (Å) *and angles* (°)

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x,y,z:

(i) $-x, 1-y, -z$ (iii) $-x, -y, 2-z$.
(ii) $x, y, 1+z$

(*a*) Intramolecular hydrogen-bond data

N(1)···N(4)	2·60 (1)
H(N1)···N(4)	2·16 (5)
N(1)–H(N1)···N(4)	105 (4)

(*b*) Selected intramolecular non-bonded distances

C(12)···N(2)	2·81 (1)	O(81)···O(82)	2·24 (1)
C(56)···N(4)	2·71 (1)	C(7)···C(3)	2·71 (1)
S(6)···N(5)	2·79 (1)	C(7)···O(81)	2·40 (1)
S(6)···O(81)	2·88 (1)	C(7)···O(82)	2·35 (1)

(*c*) Intermolecular hydrogen-bond data

$O(82)\cdots O(81)^{i}$	2·66 (1)
$H(O2)\cdots O(81)^{i}$	1·70 (6)
$O(82)–H(O2)\cdots O(81)^{i}$	160 (5)

(*d*) Selected intermolecular contacts*

$C(51)\cdots C(3)^{ii}$	3·38 (3)	$N(5)\cdots H(71)^{ii}$	2·69 (2)
$C(52)\cdots C(3)^{ii}$	3·46 (3)	$S(6)\cdots H(53)^{iii}$	2·84 (2)
$C(56)\cdots N(1)^{ii}$	3·17 (3)	$O(81)\cdots H(53)^{iii}$	2·53 (2)

* Intermolecular non-bonded separations less than the sum of the van der Waals radii.

(3) are hydrogen bonded through their carboxylic groups to form dimers. The reference molecule at x,y,z forms a dimer with the symmetry-related molecule at $-x, 1-y, -z$. The dimer has a centre of inversion between the two carboxylic groups, making the two intermolecular O–H···O hydrogen bonds equivalent. The H···O distance is 1·70 (6) Å (for a fixed O–H length of 1·00 Å) and the calculated O···O distance in the dimer is 2·66 (1) Å; this fairly short separation is accompanied by an O–H···O angle of 160 (5)° and reveals a moderately strong hydrogen bond. It may be compared with that found in the dimer of crystalline benzoic acid, where the O···O distance is 2·64 Å (Sim, Robertson & Goodwin, 1955).

As in (2) (Preuss & Gieren, 1975) the imino proton H(N1) is internally hydrogen bonded to N(4), effectively locking the molecule in the *syn,s-trans* configuration. The H(N1)···N(4) distance of 2·16 (5) Å [for a fixed N(1)–H(N1) length of 1·00 Å] is significantly less than the sum of the van der Waals radii, while the N(1)···N(4) separation is 2·60 (1) Å. This does not mean that an exceptionally strong intramolecular hydrogen bond is present, however, for the stereochemistry of the sp^2-hybridized N(1) does not allow linearity of the N(1)–H(N1)···N(4) angle. This angle is 105 (4)° and thus the hydrogen bond formed is considerably weakened. Hydrogen bonding is nevertheless favoured here by the fact that in the configuration adopted the lone pair of electrons on N(4) points towards H(N1). Consideration of the angles around N(1) (Fig. 2) indicates a definite attraction of H(N1) towards N(4). Very similar distances are found for the analogous hydrogen bond in (2) [H(N1)···N(4) 2·21; N(1)···N(4) 2·62 Å] and the angles around N(1) in (3) are identical to those found in (2) (Preuss & Gieren, 1975).

Molecular packing

A projection of the molecular packing is shown in Fig. 3, while Fig. 4 gives a stereoscopic view of the

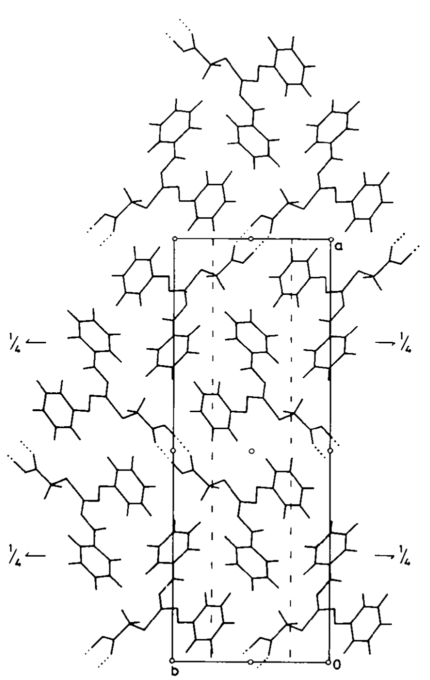

Fig. 3. Projection of the molecular packing viewed along **c**.

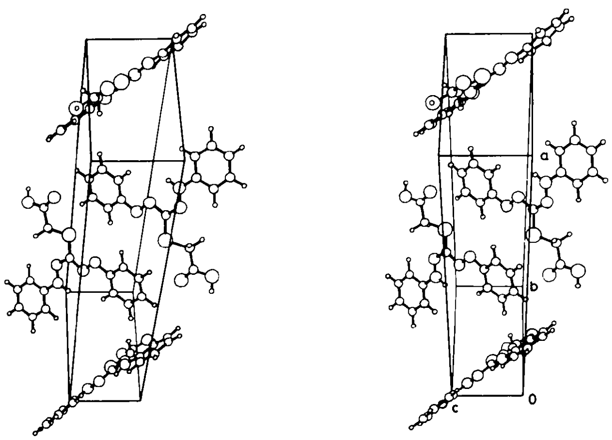

Fig. 4. Stereoscopic view of the contents of the unit cell.

contents of the cell. Selected intermolecular parameters are listed in Table 5.

The only intermolecular hydrogen bond is that between the carboxylic groups to form dimers, as discussed above. While there are several intermolecular contacts significantly less than the sum of the van der Waals radii (Table 5), it is not believed that any of these contacts has any important effect on the structure. The molecules are stacked along **c**, the plane defined in Table 3 (plane 2) forming an angle of 77·9° with the (001) plane. The interplanar distance between parallel superimposed molecules (*i.e.* between the reference molecule at x,y,z and the molecule at x, y, $1 + z$) is ~3·2 Å. This tight packing is reflected in the small average volume occupied by a non-hydrogen atom (16·8 Å^3, D_c = 1·42 Mg m^{-3}). The average volume occupied by a non-hydrogen atom in (1) is 17·2 Å^3 (D_c = 1·37 Mg m^{-3}) (Laing, 1977), while in (2) it is 17·9 Å^3 (D_c = 1·33 Mg m^{-3}) (Preuss & Gieren, 1975). The packing in (1) is tighter than that in (2) because of the strong attractive forces between partial positive and negative charges on atoms in parallel planes of the dithizone molecules (Laing, 1977). Since similarly strong electrostatic attractions cannot be invoked for either (2) or (3), the tighter packing and greater density of (3) must be directly due to dimer formation. Also, it is probably a combination of dimer formation and close interplanar packing which accounts for the low solubility of (3) in organic solvents.

Conclusion

The energetic advantages to the molecular packing in the crystal of this very planar dimer over the proposed structure in solution (5) are clear. However, why the *syn,s-trans* configuration should be preferred to the *syn,s-cis* is not obvious. The formation of a six-membered ring with a hydrogen bridge should give rise to a quasi-aromatic ring system, with an associated increase in resonance stabilization energy. However, it appears that molecular-packing considerations in the crystal are of prime importance and override possible stabilization through electronic effects within the molecule. Besides the presence of the large carboxylic group situated above the formazan ring in the proposed solution conformation (5), coplanarity of the phenyl groups with the formazan ring would be sterically impossible. These factors would create a molecular structure for which intermolecular interactions in the solid state would be difficult to minimize.

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The Structure of Chloramphenicol

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Abstract

The structure of chloramphenicol, D-(−)-*threo*-2,2-dichloro-*N*-[β-hydroxy-α-(hydroxymethyl)-*p*-nitrophenethyl]acetamide, $C_{11}H_{12}Cl_2N_2O_5$, an important broad-spectrum antibiotic, has been solved by direct methods with X-ray diffraction data collected using Mo $K\alpha$ radiation. The crystals are orthorhombic, a = 7·335 (3), b = 17·552 (8), c = 22·159 (6) Å, with space group $C222_1$, and the structure has been refined by Fourier and least-squares techniques to an R of 0·069 for 940 observed reflections. The side chain exists in the 'alicyclic' form, stabilized by hydrogen bonding between the hydroxyl groups. The dichloroacetamido moiety is folded back over the phenyl ring.

Introduction

Chloramphenicol is a widely used antibiotic produced by *Streptomyces Venezuelae* (Ehrlich, Bartz, Smith, Joslyn & Burkholder, 1947) and cultures of *Streptomyces lavendulave* (Carter, Gottlieb & Anderson, 1948). It has also been obtained synthetically by several routes (Controulis, Rebstock & Crooks, 1949; Long & Troutman, 1949). The crystal structure of chloramphenicol has been shown to be isomorphous with bromamphenicol, for which two-dimensional X-ray work has been reported (Dunitz, 1952). The present work describes the three-dimensional structure of chloramphenicol.

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Experimental

Chloramphenicol in powder form was obtained from Parke–Davis (India) Ltd, Bombay. Transparent crystalline needles were grown from ethanol. Precession and Weissenberg photographs showed the crystal system to be orthorhombic, with systematic absences hkl, $h + k = 2n + 1$; $00l$, $l = 2n + 1$ indicating the space group $C222_1$. Accurate cell parameters were obtained by least-squares treatment of the 2θ values of high-angle reflections centred on a diffractometer. The crystal density was measured by a flotation technique using bromoform and *m*-xylene. The crystal data are given in Table 1.

The crystal used for data collection, 0·32 × 0·29 × 0·36 mm, was mounted on a Picker card-automated diffractometer. Data were collected employing Nb-filtered Mo $K\alpha$ radiation within the range $2\theta \leq 49°$ using the θ–2θ scanning mode operating at 2° min^{-1} in 2θ with a scan width of 1·2° in 2θ. Individual background counts were recorded at the higher 2θ limit and three check reflections were monitored periodically for

Table 1. *Crystal data of chloramphenicol*

Chemical formula: $C_{11}H_{12}Cl_2N_2O_5$	M_r = 323·1
Crystal system and space group: orthorhombic, $C222_1$	
a = 7·335 (3) Å	Z = 8
b = 17·552 (8)	$F(000)$ = 1328
c = 22·159 (6)	λ(Mo $K\alpha$) = 0·71069 Å
d_m = 1·49 Mg m^{-3}	μ(Mo $K\alpha$) = 0·4741 mm^{-1}
d_c = 1·50	M.p. = 423 K