1,486 (6) Å et une ouverture des angles de valence correspondants: C(8)—C(9)—C(10) 129,5 (6), C(9)—C(10)—C(11) 133,1 (7)°. Ces différences déjà amorcées dans la molécule C, concernent des liaisons et des angles incluant les atomes affectés d'une très grande agitation thermique anisotrope, et sont donc la conséquence de ces vibrations: tandis que la molécule C conserve la conformation des autres molécules, la molécule D se déforme dans la région la plus flexible du cycle à sept chaînons.

Dans le cristal, les molécules A de symétrie (x, y, z) s'enchaînent aux molécules A de symétrie (−x, ±0,5 + y, −z) au moyen de liaisons hydrogène, établies entre le groupement hydroxyle OH(16) d'une molécule et l'atome d'oxygène O(17) de la molécule suivante. Il existe de même, des chaînes de molécules B, de molécules C et D; les distances O16···O17, caractéristiques de ces liaisons hydrogène, étant pour les molécules A, B, C et D respectivement de 2,828 (3), 2,980 (3), 2,890 (3) et 2,780 Å.

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Structure of the New Erythromycin Derivative V-T 108, (9S)-9,11-Dideoxy-9,11-[imino(2-acetamidoethylidene)oxy]erythromycin

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Abstract. $C_{41}H_{75}N_3O_{13}.1\cdot5CH_3OH.0\cdot5H_2O$, $M_r = 875\cdot14$, orthorhombic, $P2_12_12$, $a = 42\cdot600$ (6), $b = 14\cdot410$ (1), $c = 9\cdot268$ (2), $V = 5689$ (2) Å^3, $Z = 4$, $D_x = 1\cdot015$ g cm^{-3}, $\lambda(\text{Cu} K\alpha) = 1\cdot5418$ Å, $\mu = 6\cdot37$ cm^{-1}, $F(000) = 1912$, $T = 293$ K, $R = 7\cdot3\%$ for 4716 observed reflections. The asymmetric C atoms C(9) and C(90) have S configurations. The six-membered 9,11-oxazine ring has an unusual twist conformation. Two intramolecular hydrogen bonds N(9)—H(9N)···O(60) and N(92)—H(92)···O(10) exist, which have never been observed in any previously investigated erythromycin derivative. A further quasi-intramolecular hydrogen bond is formed *via* one of the solvent methanol molecules.

Introduction. Erythromycin is the most widely used macrolide antibiotic mainly acting against Gram-positive bacteria. However, it is weakly active against Gram-negative organisms and its pharmacokinetics are not satisfactory. With the aim of improving both properties, tetrahydro-1,3-oxazine derivatives (2) were synthesized by condensation of (9S)-erythromycylamine (1) with substituted acetaldehydes.

(1)

R-CH₂-CHO
⟶
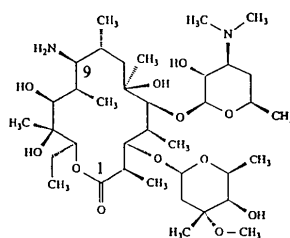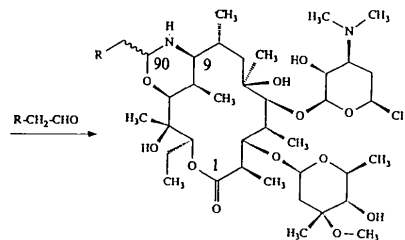
(2)

Dirithromycin (3): R = CH₃O(CH₂)₂O—
V-T 108 (4): R = CH₃CONH—

During the condensation, a new chiral centre is formed at C(90) of the oxazine ring (Maier, Woitun, Wetzel & Lechner, 1988; Firl, Prox, Luger, Maier, Woitun & Daneck, 1990). In case of dirithromycin (3), the R configuration was determined by X-ray analysis (Luger & Maier, 1979). V-T 108 (4) is the second member of this series with interesting biological properties. Investigations by TLC and NMR suggest that V-T 108 has an S configuration at C(90). To confirm the structure and configuration of V-T 108 an X-ray analysis was carried out.

Experimental. Colorless prismatic crystals from methanol. Crystal preparation was extremely difficult because of immediate decomposition when removed from the solvent. The crystal used for X-ray measurements ($0.80 \times 0.58 \times 0.25$ mm) was mounted in a glass capillary together with a drop of methanol. Under these conditions the crystal was stable for sufficient time. Crystal growth in acetonitrile affords a second orthorhombic modification [$a = 18.240$ (9), $b = 23.401$ (6), $c = 23.590$ (9) Å, $V = 10.064$ (7) Å^3, space group probably $P2_12_12_1$ or $P2_12_12$]. Since that cell is twice the volume of the methanol modification no structure determination was attempted. So all further data reported here are for the methanol modification. DEC MicroPDP11-controlled Stoe four-circle diffractometer, Ni-filtered Cu $K\alpha$ radiation, lattice parameters from 30 high-order reflections ($25 \le \theta \le 40°$). One octant ($0 \le h \le 49, 0 \le k \le 16, 0 \le l \le 10$) of independent reflections measured, ω–2θ scan, $(\sin\theta/\lambda)_{max} = 0.585$ Å^{-1}, 5205 reflections, 489 unobserved [$I < 2\sigma(I)$], two standard reflections indicated an average intensity decrease of 15%, for which correction was made. Since the decrease of intensity was rather different for both reference reflections, the correction by a common linear scale factor is only a crude approximation of the intensity variation owing to crystal decay.

Phase problem solved with direct methods (*MITHRIL*; Gilmore, 1983). The trials with the highest combined figures of merit in the subprograms *TANGEN*, *MAGEX* and *RANTAN* showed almost the complete molecular structure. 52 of the 57 non-H atoms were identified, the missing atoms were located from a subsequent difference synthesis. In addition, five heavy-atom peaks were present of which two pairs were identified as C and O atoms of two methanol molecules and the last one as a water O atom. Since the peaks of the first methanol molecule had twice the height of the last three, the population parameters of the second methanol and the water molecule were estimated to be 0.5. Hence, this unit cell of V-T 108 has one and a half molecules of methanol and half a molecule of water as solvent in its asymmetric unit. This interpretation is supported by the integration of the solvent molecules in hydrogen bonds as discussed below.

Least-squares refinement with isotropic, then with anisotropic temperature factors for non-H atoms; H atoms (about 50% located from difference synthesis, further ones calculated from chemical considerations, no H atoms determined on solvent molecules) refined isotropically (*XRAY*76; Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Quantity minimized $\Sigma w(|F_o| - |F_c|)^2$, with $w = xy$, $x = 1$ for $\sin\theta > 0.7$, $x = (\sin\theta/0.7)$ for $\sin\theta \le 0.7$, $y = 1$ if $|F_o| < 2.5$ and $y = 2.5/|F_o|$ otherwise. Parameters for w were chosen so as to make $w\Delta F$ almost independent of $|F_o|$ and $\sin\theta$. Unobserved reflections included only if $|F_c| > |F_o|$; atomic scattering factors from the standard routine of *XRAY*76 (Cromer & Mann, 1968; Stewart, Davidson & Simpson, 1965). After convergence $R = 7.3$, $wR = 9.3\%$ for observed reflections; $(\Delta/\sigma)_{max} = 1.6$ (x, y coordinates of water oxygen), $(\Delta/\sigma)_{av} = 0.2$; $\Delta\rho_{max} = 0.58$, $\Delta\rho_{min} = -0.47$ e Å^{-3} in final difference synthesis. All calculations on a CDC Cyber 175 computer. Moderate agreement factors obviously due to the above-mentioned intensity scaling problem and disorder of solvent molecules.

Discussion. Fractional coordinates and equivalent isotropic temperature factors (Hamilton, 1959) of V-T 108 are listed in Table 1.* Bond lengths and the atomic numbering scheme, which was chosen in accordance with the previously investigated erythromycin derivative dirithromycin (3) (Luger & Maier, 1979), can be taken from Fig. 1. A stereoview (*SCHAKAL*; Keller, 1980) of the molecular structure is given in Fig. 2(a); bond angles and selected torsion angles have been deposited (see deposition footnote).

Bond lengths and angles are as expected and need no detailed discussion. It should only be mentioned that the lactone O—C bond O(14)—C(1) is rather short [1.336 (4) Å] as is usually found for this group. The C=O bond C(1)—O(10) has a normal length of 1.200 (5) Å. The C=O bond C(93)—O(93) of the amide group is lengthened to 1.236 (7) Å. However, both carbonyl groups are involved in hydrogen bonds, causing generally longer C=O bonds. The amide N atom N(92) is in a planar configuration; the two other nitrogens N(9) and N(30″) both have pyrimidal arrangements as can be seen from Fig. 2 and the bond angles which are significantly below 120° for the last two atoms.

Table 1. *Fractional atomic coordinates of V-T 108 with* U_{eq} (Å² × 10²) *values calculated after Hamilton* (1959)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

|	x	y	z	U_{eq}
C(1)	0·69296 (9)	0·3452 (3)	0·6595 (5)	5·9 (1)
O(10)	0·71687 (8)	0·3486 (2)	0·7277 (5)	8·5 (1)
C(2)	0·6787 (1)	0·4268 (3)	0·5800 (5)	6·0 (1)
C(20)	0·7043 (1)	0·4677 (4)	0·4856 (7)	8·2 (2)
C(3)	0·66482 (8)	0·4962 (2)	0·6914 (4)	5·4 (1)
O(30)	0·65981 (7)	0·5861 (2)	0·6268 (3)	6·49 (9)
C(4)	0·63330 (9)	0·4604 (3)	0·7516 (5)	6·1 (1)
C(40)	0·6087 (1)	0·4538 (7)	0·6323 (8)	9·7 (2)
C(5)	0·62241 (8)	0·5184 (2)	0·8849 (5)	5·8 (1)
O(50)	0·58876 (6)	0·5231 (2)	0·8952 (4)	6·64 (9)
C(6)	0·63401 (9)	0·4791 (3)	1·0305 (5)	6·0 (1)
O(60)	0·66686 (6)	0·4577 (2)	1·0157 (4)	6·53 (9)
C(60)	0·6295 (1)	0·5511 (3)	1·1488 (7)	7·4 (2)
C(7)	0·61686 (9)	0·3882 (3)	1·0695 (5)	6·2 (1)
C(8)	0·6255 (1)	0·3380 (3)	1·2099 (5)	6·8 (1)
C(80)	0·5961 (2)	0·2948 (5)	1·2750 (8)	9·4 (2)
C(9)	0·6511 (1)	0·2620 (3)	1·1975 (5)	6·6 (1)
C(10)	0·6448 (1)	0·1878 (3)	1·0786 (5)	6·5 (1)
C(100)	0·6457 (2)	0·0892 (3)	1·1457 (8)	8·9 (2)
N(9)	0·68228 (8)	0·3025 (3)	1·1876 (4)	6·3 (1)
C(90)	0·70575 (9)	0·2388 (3)	1·1453 (5)	6·2 (1)
C(91)	0·7383 (1)	0·2815 (3)	1·1406 (6)	7·1 (1)
N(92)	0·74119 (8)	0·3502 (3)	1·0260 (5)	7·1 (1)
C(93)	0·7584 (1)	0·4273 (3)	1·0391 (6)	7·3 (1)
O(93)	0·77091 (9)	0·4521 (3)	1·1529 (5)	9·0 (1)
C(94)	0·7629 (2)	0·4825 (5)	0·9023 (8)	9·5 (2)
O(110)	0·69976 (6)	0·1955 (2)	1·0049 (3)	6·02 (8)
C(11)	0·66793 (8)	0·2049 (3)	0·9549 (5)	5·8 (1)
C(12)	0·66445 (9)	0·1457 (2)	0·8190 (5)	5·9 (1)
O(120)	0·67162 (8)	0·0502 (2)	0·8490 (4)	6·8 (1)
C(120)	0·6310 (1)	0·1477 (3)	0·7630 (6)	7·2 (1)
C(13)	0·6881 (1)	0·1807 (3)	0·7044 (5)	6·2 (1)
C(130)	0·6935 (2)	0·1154 (3)	0·5795 (7)	8·7 (2)
C(131)	0·7233 (2)	0·1417 (8)	0·4989 (8)	12·2 (3)
O(14)	0·67603 (6)	0·2677 (2)	0·6455 (3)	6·11 (8)
C(1')	0·6839 (1)	0·6512 (3)	0·6531 (6)	7·4 (1)
C(2')	0·6847 (2)	0·7220 (4)	0·5325 (8)	10·5 (3)
C(3')	0·6597 (2)	0·7993 (3)	0·5415 (7)	10·1 (3)
C(30')	0·6667 (5)	0·8720 (5)	0·425 (1)	15·2 (6)
O(30')	0·6285 (1)	0·7652 (3)	0·5356 (5)	11·3 (2)
C(31')	0·6187 (6)	0·7177 (8)	0·410 (2)	18·9 (8)
C(4')	0·6624 (1)	0·8418 (3)	0·6899 (6)	8·1 (2)
O(40')	0·6393 (1)	0·9120 (2)	0·7073 (5)	9·8 (1)
C(5')	0·6574 (1)	0·7675 (3)	0·8074 (6)	7·1 (1)
C(50')	0·6624 (1)	0·8061 (4)	0·9552 (7)	8·2 (2)
O(5')	0·68099 (7)	0·6941 (2)	0·7909 (4)	7·04 (9)
C(1'')	0·5743 (1)	0·6045 (3)	0·8513 (8)	7·7 (2)
C(2'')	0·5397 (1)	0·5845 (3)	0·8354 (8)	8·1 (2)
O(20'')	0·53482 (9)	0·5221 (3)	0·7176 (6)	9·5 (1)
C(3'')	0·5208 (1)	0·6728 (4)	0·811 (1)	10·1 (3)
N(30'')	0·4866 (1)	0·6500 (4)	0·810 (1)	12·6 (3)
C(31'')	0·4721 (2)	0·6483 (8)	0·950 (2)	15·7 (6)
C(32'')	0·4693 (3)	0·7150 (9)	0·724 (3)	21· (1)
C(4'')	0·5304 (1)	0·7481 (5)	0·917 (2)	11·8 (4)
C(5'')	0·5657 (1)	0·7604 (4)	0·921 (1)	11·4 (3)
C(50'')	0·5763 (2)	0·8309 (7)	1·025 (2)	17·0 (8)
O(5'')	0·58005 (8)	0·6732 (2)	0·9559 (6)	9·1 (1)
O(1M)	0·7055 (1)	0·6062 (3)	1·0275 (6)	10·7 (2)
C(1M)	0·7200 (2)	0·6486 (6)	1·1509 (8)	10·8 (2)
O(2M)	0·5309 (5)	0·592 (1)	0·437 (2)	17·6 (7)
C(2M)	0·5429 (5)	0·538 (2)	0·337 (3)	17· (1)
O(1W)	0·5779 (4)	0·933 (2)	0·589 (3)	23· (1)
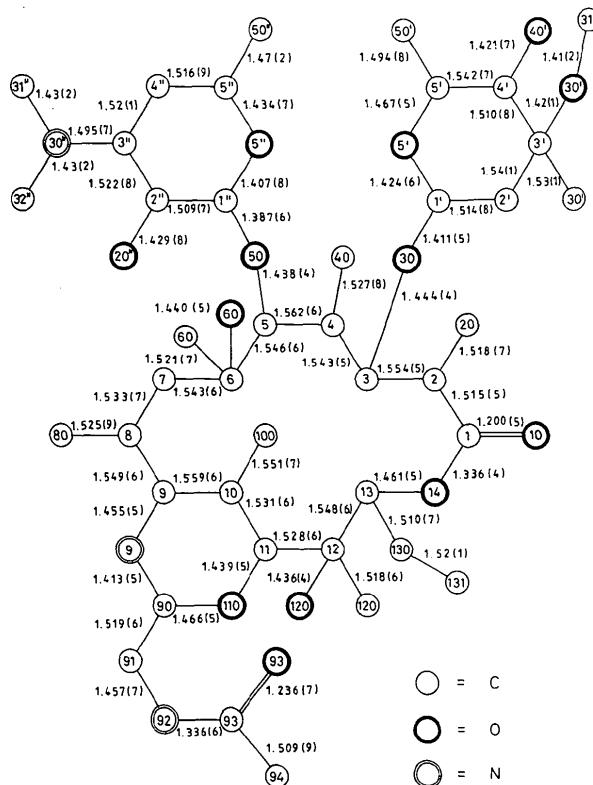
Fig. 1. Atomic numbering scheme and bond lengths (Å, e.s.d.'s in parentheses) for V-T 108.

The molecular structure of erythromycin consists of a 14-membered lactone ring (atoms 1 to 14) and two sugar residues cladinose (primed atoms) and desosamine (double-primed atoms). In the present structure [and also in the analogous derivative dirithromycin (3)] an additional ring is present at the macrocycle. Fig. 2 clearly shows that it is a six-membered ring so that V-T 108 has a 9,11-oxazine structure as was also found for dirithromycin (3).
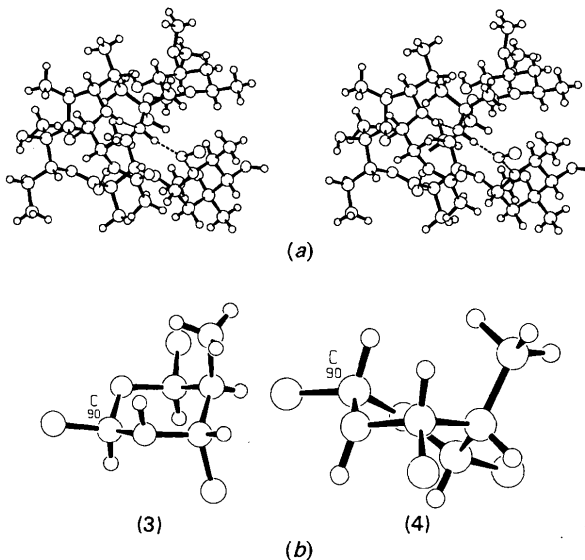
Fig. 2. (a) Stereoview of the molecular structure of V-T 108 (*SCHAKAL*; Keller, 1980). Intramolecular hydrogen bonds are drawn in dotted lines, the contributing methanol molecule is also shown. (b) Oxazine rings of dirithromycin (3) in chair conformation [C(90) in an R configuration] and of V-T 108 (4) in twist conformation [C(90) in an S configuration].

Table 2. *Cremer–Pople puckering parameters of the six-membered ring and comparison with theoretical values*

Ring	Q (Å)	θ (°)	φ (°)
9,11-Oxazine	0·714 (8)	88·1 (7)	78·9 (9)
$^5S_1$ (theoretical)	–	90	90
$B_{1,4}$ (theoretical)	–	90	60
Cladinose	0·547 (7)	168·6 (8)	60· (1)
$^1C_4$ (theoretical)	–	180	Undetermined
Desosamine	0·536 (7)	6·1 (7)	336· (2)
$^4C_1$ (theoretical)	–	0	Undetermined

Table 3. *Summary of hydrogen bonds*

X—H⋯Y	X⋯Y (Å)	X—H (Å)	H⋯Y (Å)	Symmetry operation for Y
N(92)—H(92)⋯O(10)	2·925 (6)	1·00 (7)	1·96 (7)	x, y, z
N(9)—H(9N)⋯O(60)	2·823 (5)	0·81 (6)	2·07 (6)	x, y, z
O(60)—H(60)⋯O(1M)	2·704 (5)	0·95 (6)	1·77 (6)	x, y, z
O(20″)—H(20″)⋯O(2M)	2·79 (2)	1·01 (12)	1·96 (12)	x, y, z
O(1W)—H(1W)*⋯O(40′)	2·86 (2)	–*	–*	x, y, z
O(1M)—H(1M)*⋯O(5′)	2·740 (6)	–*	–*	x, y, z
O(40′)—H(40′)⋯O(120')	2·754 (5)	1·02 (6)	1·74 (6)	$x, 1 + y, z$
O(120)—H(120)⋯O(93ii)	2·827 (5)	0·86 (6)	2·04 (6)	$\frac{3}{2}-x, -\frac{1}{2}+y, 2-z$

* The corresponding H atom could not be located.

The conformation and configuration of this oxazine ring is of special interest with respect to the interpretation of NMR data of this compound and also in comparison with dirithromycin. Since the absolute configuration of the molecule can be deduced from the known configuration of the sugar residues (cladinose belongs to the L, desosamine to the D series), the absolute form of the asymmetric carbon atoms C(9) and C(90) can be assigned. Fig. 2 shows that C(9) has an S configuration as in (3); C(90) also has an S configuration in the present structure, but was R in (3), so that the absolute configuration has changed at this C atom.

Fig. 2(*b*) also shows that the oxazine six-membered ring, which had a normal chair form for dirithromycin, now has an unusual conformation. From the Cremer–Pople puckering parameters (Cremer & Pople, 1975; Luger & Bülow, 1983) this conformation can be designated as twist form $^5S_1$ with a tendency towards a boat form $B_{1,4}$ based on a choice of C(11), C(10)... *etc.* as ring atoms 1, 2... (see Table 2). For the twist form, the ring atoms 1 and 5, *i.e.* C(11) and C(90) are the out-of-plane atoms; for the boat form $B_{1,4}$, C(11) and N(9) represent the bow and stern of the boat.

This unusual ring conformation and the S configuration of C(90) cause a spatial arrangement for N(9) and the amide group which allows two intramolecular hydrogen bonds N(9)—H(9N)—O(60) and N(92)—H(92)—O(10) (see Table 3). Neither of these hydrogen bonds have been observed in dirithromycin. In the molecular structure of that compound the (somewhat chemically different) side chain at C(90) is directed away from the macrocycle, whereas the side-chain amide group of V-T 108 is situated above the 14-membered ring.

Moreover, an additional quasi-intramolecular hydrogen bond exists wherein the OH group at C(6) is connected *via* the methanol molecule 1 to O(5′), established by two hydrogen bonds [O(60)—H(60)⋯O(1M)—H(1M)⋯O(5′), see Table 3]. So the molecule of V-T 108 has a rather globular overall shape with most of its active groups (N—H and O—H) shielded by intramolecular interactions. Only OH groups of the sugar residues and O(120)—H are still available for intermolecular contacts.

Owing to the non-chair geometry of the oxaxine ring the substituents of this ring have unusual positions. Of the non-H-atom substituents, C(100) is in an axial position, C(12) and C(91) are in equatorial positions and C(8) is in a bisectional position.

The conformations of the two sugar residues are as expected. Both six-membered rings have almost undistorted chair forms (see Table 2), cladinose is in the $^1C_4$ (L) conformation, desosamine is in the $^4C_1$ (D) form. The glycosidic linkages to the macrocycles are α for cladinosine and β for desosamine. Nevertheless, the relative orientations along the glycosidic linkages are comparable for both residues wherein C(3) as well as C(5) are in *gauche* positions with respect to the sugar ring O atoms [O(5′) and O(5″) respectively] and *trans* with respect to ring atoms 2 [C(20′) and C(20″)]. This arrangement was the same for dirithromycin and seems to be the energetically favoured one. A rough molecular mechanics calculation with a force field [implemented in *CHEMX* (Davies, 1980)] not parametrized for the *exo* anomeric effect was executed with the torsion angles along C(3)—O(30) and O(30)—C(1′) (and analogous for desosamine) systematically varied. Sharp minima at the X-ray positions confirmed the preference of this conformation.

A survey over all hydrogen bonds of this structure is given in Table 3. Except for the solvent molecules with population parameters of 0·5 all donor groups (—OH and —NH) are engaged in hydrogen bonds. In addition to the already mentioned intra- and quasi-intramolecular bonds two intermolecular hydrogen bonds O(120)—H(120)⋯O(93ii) and
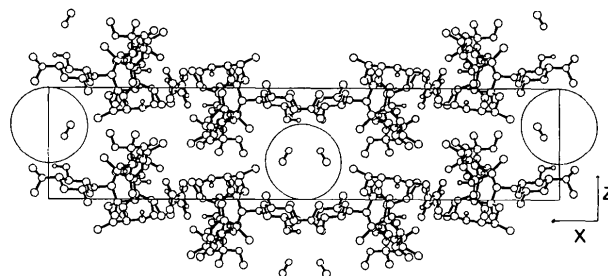

Fig. 3. Unit cell projected down the y axis. The large circles indicate the rather empty channels in the y direction.

O(40′)—H(40′)···O(120^i) exist which connect symmetry-related molecules mainly in the y direction.

Fig. 3, representing a projection of the unit cell in the y direction, shows that at $x = 0$, 1/2, ... relatively empty spaces are present, forming channels in the y direction with diameters of about 6 Å. Inside the channels there are only the half-populated methanol molecules, on the border there are the half-populated water molecules. Both of these solvent molecules take part in one hydrogen bond each [the water molecule O(1W) as donor, the methanol oxygen O(2M) as acceptor, see Table 3]. Since both molecules are not engaged in any further hydrogen bonding (although they have free donor groups) and since they are located at rather empty sites of the crystal lattice it becomes understandable that they are less strongly integrated in the crystal packing and may get out quite easily. If, however, a considerable amount of methanol is withdrawn from the channels the crystal lattice is no longer stable which then causes the rapid decomposition of the crystal, when removed from the solvent. So the microscopic properties of this crystal lattice may serve as an explanation for the macroscopically observed decay of the crystal. Also in connection with this the unusual low density, close to 1 g cm^{-3}, should be

mentioned. In comparable organic compounds the density is between 1·2 and 1·3 g cm^{-3}, for example 1·20 for dirithromycin or 1·24 g cm^{-3} for erythromycin A carbonate (Hempel, 1978). This is a further hint of the instability of the crystals.

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A New Crystal Structure of 3,6-Diphenylpyrrolo[3,4-c]pyrrole-1,4-dithione

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Abstract. $C_{18}H_{12}N_2S_2$, $M_r = 320·426$, monoclinic, $C2/c$, $a = 27·008$ (4), $b = 6·982$ (1), $c = 7·935$ (1) Å, $\beta = 100·64$ (1)°, $V = 1470·6$ (7) Å^3, $Z = 4$, $D_x = 1·447$, $D_m = 1·436$ Mg m^{-3}, graphite-monochromatized Cu $K\alpha$ radiation, $\lambda = 1·5418$ Å, $\mu = 3·18$ mm^{-1}, $T = 293$ K, $F(000) = 664$, $R = 0·064$ for 1496 reflec-

tions. The molecule has C_2 symmetry. Both phenyl rings are twisted, in opposite directions, out of the plane of the heterocyclic ring system by 30·1 (2)°. The heterocyclic ring system is not quite planar, as the two five-membered rings form a dihedral angle of 5·4 (1)°. Along the stacking axis, alternate molecules lie directly above each other, forming columns. The molecules in adjacent columns overlap only at the S—C(1), C(1)—N, N—C(3) and N—H bonds in one

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