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The Structure of 5-Benzyl-2-phenyl-4-tolylthiazole

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$C_{23}H_{19}NS$, monoclinic, $P2_1/c$, $a = 10{\cdot}789\,(7)$, $b = 9{\cdot}803\,(9)$, $c = 17{\cdot}375\,(11)$ Å, $\beta = 93{\cdot}90\,(10)°$, $V = 1833{\cdot}4$ Å^3, $Z = 4$, $D_c = 1{\cdot}24$, $D_o = 1{\cdot}23$ g cm^{-3}, $R = 0{\cdot}051$, 1343 reflexions. The dimensions of the molecule have been determined by X-ray diffraction and are compared with those in similar molecules. Bond lengths show that the molecule has the principal resonance structure 5-benzyl-2-phenyl-4-tolythiazole, but there is considerable resonance interaction with mesoionic contributors. The atoms of the thiazole ring are almost coplanar with those of the phenyl ring, whereas the dihedral angle between the thiazole and tolyl rings is 29°.

Introduction

In the course of a study of heterocyclic organic compounds containing S and N, a compound analysed as $C_{23}H_{19}NS$ was synthesized. The molecular conformation and crystal structure of this product, 5-benzyl-2-phenyl-4-tolylthiazole, have now been determined by X-ray crystal structure analysis. The main structural interest in the compound centres on the state of conjugation in the five-membered ring, its geometry and conformation.

Experimental

The preliminary cell parameters and space group were obtained from Weissenberg photographs. A small colourless crystal was then mounted on a Picker FACS-1 four-circle computer-controlled diffractometer equipped with a scintillation counter and a pulse-height analyser. The accurate cell dimensions and orientation matrix were obtained by a least-squares fit of χ, φ, ω and 2θ values from 12 independent reflexions.

Crystal data

$C_{23}H_{19}NS$, $M_r = 341{\cdot}48$, monoclinic, $a = 10{\cdot}789\,(7)$, $b = 9{\cdot}803\,(9)$, $c = 17{\cdot}375\,(11)$ Å, $\beta = 93{\cdot}90\,(10)°$, $V = 1833{\cdot}4$ Å^3, $Z = 4$, $D_o = 1{\cdot}23$, $D_c = 1{\cdot}24$ g cm^{-3}; space group $P2_1/c$ from systematic absences: $0k0$ for k odd, $h0l$ for l odd.

A crystal 0·3 × 0·3 × 0·4 mm was chosen to obtain the intensity data on the diffractometer with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) up to $2\theta = 50°$. The moving-crystal–moving-counter technique was used with a 2θ scan rate of 1° min^{-1} and a scan range of 2·0–2·5° in order to properly account for the separation of the $K\alpha_1$ and $K\alpha_2$ peaks at various 2θ values. Background counts of 10 s were measured at each end of every 2θ scan. During the data collection three standards, measured before every 50 reflexions, showed small fluctuations not exceeding 5%. Of the 3208 independent reflexions measured, 1342 were considered observed and had $I > 1{\cdot}40\sigma$ $\{\sigma = [N_s + (t_s/t_b)^2N_b]^{1/2}$, where N_s is the total peak count during the time of scanning t_s, and t_b is the time spent in measuring the N_b background counts$\}$. An arbitrary intensity equal to 0·5 times the observable limit was assigned to the non-observed reflexions. All intensities were corrected for Lorentz and polarization effects but not for absorption as [μ(Mo $K\alpha$) = 1·44 cm^{-1}].

The structure was solved both by the heavy-atom method and by direct methods. A three-dimensional Patterson map permitted location of the S atom. A Fourier map phased on this atom showed the positions of some of the non-hydrogen atoms. The coordinates of the complete skeleton were defined by successive Fourier maps.

A similar structure was obtained using the multisolution tangent refinement method *MULTAN* (Germain, Main & Woolfson, 1971) with 150 $|E| > 2{\cdot}05$ and 50 weak reflexions (for the definition of the ψ_0 figure of merit). The number of phase relationships found was 677. The automatically chosen starting set is reported in Table 1. Of the four possible solutions provided by the program, according to values $(0,\pi)$ of the phase angles A and B, the correct one stood out as having the highest value of ABSFOM and the lowest values of RESID and ψ_0. The corresponding phase angles A and B were 0 and π, respectively, and the phase angles of all 150 reflexions were coincident with the values previously calculated from the structure derived by means of the heavy-atom method. The positional and isotropic thermal parameters of the non-hydrogen atoms were refined to $R\ [=(\sum||F_o|-|F_c||)/\sum|F_o|\,]=0\cdot12$ by several cycles of block-diagonal least squares minimizing the function $\Delta=\sum w(|F_o|-|F_c|)^2$ according to the program of Immirzi (1967). Atomic scattering factors were calculated from the expression given by Vand, Eiland & Pepinsky (1957) using the values for the parameters given by Moore (1963). The weighting scheme $1/w=A+B|F_o|+C|F_o|^2$ was adopted (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961), where $A=2\ F_o(\text{min.})$, $B=1\cdot0$ and $C=2/F_o(\text{max.})$. After an anisotropic refinement the H atoms were introduced in the calculations in fixed positions with their coordinates being defined on stereochemical grounds and in agreement with a ΔF synthesis. The B value assumed for all H atoms was 5·0 Å^2. Refinement then converged to $R=0\cdot051$ for the 1342 non-zero reflections. The final shifts of the atomic parameters were negligible and were all below the corresponding σ.

Table 1. *Starting set for the tangent formula*

h k l	$\vert E\vert$	Phase	
10 0 $\bar{4}$	2·28	0	$\sum_1$ ($p=0\cdot997$)
7 2 $\overline{10}$	4·59	0	Origin fixing
1 1 3	3·77	0	
1 2 $\bar{3}$	3·61	0	
2 10 $\overline{10}$	3·65	*A*	
1 5 $\overline{11}$	3·22	*B*	

Table 2. *Final fractional coordinates with e.s.d.'s in parentheses*

	x	*y*	*z*
S	0·26971 (12)	0·20513 (13)	0·15015 (8)
N	0·4039 (3)	−0·0027 (4)	0·1878 (2)
C(1)	0·2964 (4)	0·0513 (5)	0·1994 (3)
C(2)	0·4695 (4)	0·0730 (5)	0·1374 (2)
C(3)	0·4127 (4)	0·1914 (5)	0·1105 (3)
C(4)	0·4534 (5)	0·2981 (5)	0·0546 (3)
C(5)	0·3960 (4)	0·4380 (5)	0·0677 (3)
C(6)	0·4505 (5)	0·5247 (5)	0·1214 (3)
C(7)	0·3977 (6)	0·6514 (6)	0·1366 (3)
C(8)	0·2881 (6)	0·6880 (6)	0·0978 (3)
C(9)	0·2323 (5)	0·6028 (6)	0·0428 (3)
C(10)	0·2850 (5)	0·4750 (6)	0·0271 (3)
C(11)	0·5932 (4)	0·0217 (5)	0·1187 (3)
C(12)	0·6446 (4)	0·0473 (5)	0·0484 (3)
C(13)	0·7589 (5)	−0·0091 (5)	0·0325 (3)
C(14)	0·8262 (5)	−0·0895 (5)	0·0869 (3)
C(15)	0·7749 (5)	−0·1130 (6)	0·1566 (3)
C(16)	0·6608 (5)	−0·0602 (6)	0·1729 (3)
C(17)	0·2045 (4)	−0·0065 (5)	0·2495 (3)
C(18)	0·2351 (5)	−0·1298 (5)	0·2883 (3)
C(19)	0·1505 (5)	−0·1834 (6)	0·3370 (3)
C(20)	0·0393 (5)	−0·1210 (7)	0·3477 (3)
C(21)	0·0086 (5)	−0·0009 (6)	0·3076 (3)
C(22)	0·0911 (5)	0·0554 (6)	0·2587 (3)
C(23)	0·9508 (6)	−0·1505 (7)	0·0703 (4)
H(4)	0·555	0·309	0·062
H(41)	0·430	0·266	−0·004
H(6)	0·536	0·494	0·154
H(7)	0·444	0·721	0·179
H(8)	0·243	0·785	0·110
H(9)	0·146	0·634	0·010
H(10)	0·241	0·406	−0·015
H(12)	0·593	0·111	0·006
H(13)	0·797	0·010	−0·024
H(15)	0·829	−0·173	0·199
H(16)	0·623	−0·080	0·229
H(18)	0·323	−0·181	0·280
H(19)	0·174	−0·279	0·368
H(20)	−0·025	−0·164	0·388
H(21)	−0·081	0·050	0·317
H(22)	0·068	0·149	0·227
H(23)	0·989	−0·207	0·119
H(231)	1·016	−0·068	0·058
H(232)	0·941	−0·216	0·020

The final fractional coordinates and the corresponding standard deviations of the atoms of the independent unit are listed in Table 2.* All calculations were performed on the Univac 1106 computer of this Institute using a local program set.

Results and discussion

The molecular and crystal structures of 5-benzyl-2-phenyl-4-tolylthiazole (I) are displayed in Figs. 1 and 2 (*ORTEP*, Johnson, 1970). The bond data of the molecule with the estimated standard deviations are reported in Table 3. The geometry of the molecule can be described in terms of four planes through the four ring systems (Table 4). R.m.s. distances are approximately 0·010 Å in each case and therefore all rings are essentially planar. C(4), C(11) and C(17) deviate 0·033, 0·001 and 0·017 Å from the five-membered-ring plane. The values of the smallest torsional angles around the C(1)–C(17) bond are 0·3 and 1·7°. The

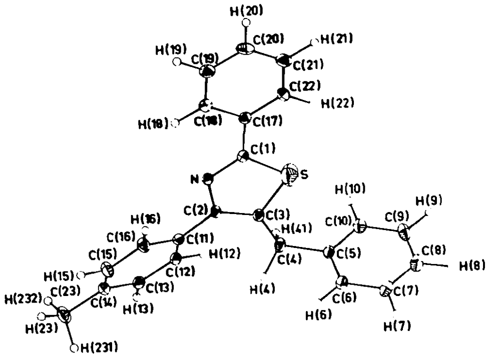

Fig. 1. The molecule of 5-benzyl-2-phenyl-4-tolylthiazole, showing the atom-labelling scheme and 30% probability thermal vibration ellipsoids (Johnson, 1970).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33819 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

small dihedral angle between the thiazole ring and the phenyl group C(17)—C(22) (1·5°) is noticeable, especially if account is taken of the presence of the lone pairs on the N and S atoms, and indicates that resonance and lattice-energy terms predominate for these two rings. The dihedral angle between the thiazole ring and the tolyl group C(11)—C(16) is 29°, while the smallest torsional angles about the C(2)—C(11) bond are −26·9 and −30·9°. Some residual resonance interaction may still be expected here. The relatively large dihedral angle between the thiazole and tolyl rings is the result of steric interaction between the tolyl and benzyl moieties, in particular between H(4) and H(12). The distance between these atoms is 2·22 Å, but would only be 1·58 Å if no torsional relief was applied. Similarly, the H(12)· · · C(4) distance of 2·55 Å would be 2·32 Å in the case of perfect co-planarity. As a result of the steric interaction the C(3)—C(2)—C(11) and C(2)—C(3)—C(4) angles are both opened up (to 126·7 and 131·1° respectively). The same also applies to C(2)—C(11)—C(12) (123·2°). Steric crowding cannot be applied to explain the 3·5° difference in exocyclic angles at C(1). However, as is well known, the bond angles about a trigonal C atom ($R^1R^2C{=}X$) are far from being equal, with a tendency to a small angle opposite the double bond (*i.e.* $\angle R^1{-}C{-}R^2$). Therefore, with the double-bond character of the N—C(1) bond, S—C(1)—C(17) should be smaller than N—C(1)—C(17), as observed. The same applies to the exocyclic bond angles of C(2)=C(3). The distribution of the bond angles at C(17) is probably a consequence

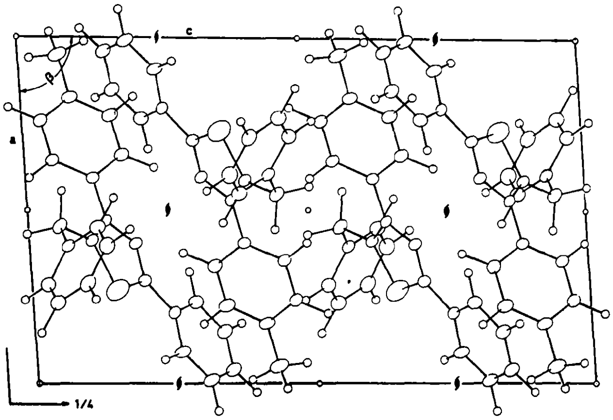


Fig. 2. Structure of 5-benzyl-2-phenyl-4-tolylthiazole viewed down the *b* axis.

Table 3. *Most significant bond data*

(*a*) Bond lengths (Å)

S—C(1)	1·748 (5)	C(3)—C(4)	1·513 (7)	C(2)—C(11)	1·483 (6)	C(1)—C(17)	1·476 (6)
S—C(3)	1·737 (4)	C(4)—C(5)	1·529 (7)	C(11)—C(12)	1·396 (6)	C(17)—C(18)	1·413 (7)
N—C(1)	1·303 (6)	C(5)—C(6)	1·365 (7)	C(11)—C(16)	1·403 (7)	C(18)—C(19)	1·389 (8)
N—C(2)	1·380 (6)	C(5)—C(10)	1·395 (7)	C(12)—C(13)	1·396 (7)	C(19)—C(20)	1·371 (8)
C(2)—C(3)	1·379 (6)	C(6)—C(7)	1·399 (8)	C(13)—C(14)	1·396 (7)	C(20)—C(21)	1·396 (9)
		C(7)—C(8)	1·368 (9)	C(14)—C(15)	1·384 (8)	C(21)—C(22)	1·386 (8)
		C(8)—C(9)	1·376 (8)	C(15)—C(16)	1·383 (8)	C(22)—C(17)	1·384 (7)
		C(9)—C(10)	1·410 (8)	C(14)—C(23)	1·516 (8)		

(*b*) Bond angles (°)

S—C(1)—N	113·2 (2)	Ç(6)—C(5)—C(10)	119·9 (2)	C(12)—C(11)—C(16)	118·1 (2)	N—C(1)—C(17)	125·2 (2)
C(1)—N—C(2)	112·4 (2)	C(5)—C(6)—C(7)	121·3 (2)	C(11)—C(12)—C(13)	120·7 (2)	S—C(1)—C(17)	121·6 (2)
N—C(2)—C(3)	115·6 (2)	C(6)—C(7)—C(8)	119·3 (3)	C(12)—C(13)—C(14)	120·9 (2)	C(1)—C(17)—C(18)	117·7 (2)
S—C(3)—C(2)	108·5 (2)	C(7)—C(8)—C(9)	120·3 (3)	C(13)—C(14)—C(15)	117·8 (3)	C(1)—C(17)—C(22)	122·3 (2)
C(1)—S—C(3)	90·4 (1)	C(8)—C(9)—C(10)	120·7 (3)	C(14)—C(15)—C(16)	122·1 (3)	C(18)—C(17)—C(22)	119·9 (2)
S—C(3)—C(4)	120·4 (2)	C(5)—C(10)—C(9)	118·5 (3)	C(11)—C(16)—C(15)	120·4 (3)	C(17)—C(18)—C(19)	118·2 (3)
C(2)—C(3)—C(4)	131·1 (2)	N—C(2)—C(11)	117·7 (2)	C(15)—C(14)—C(23)	120·8 (2)	C(18)—C(19)—C(20)	122·0 (3)
C(3)—C(4)—C(5)	112·7 (2)	C(3)—C(2)—C(11)	126·7 (2)	C(13)—C(14)—C(23)	121·4 (2)	C(19)—C(20)—C(21)	119·3 (3)
C(4)—C(5)—C(6)	120·0 (3)	C(2)—C(11)—C(12)	123·2 (2)			C(20)—C(21)—C(22)	120·1 (3)
C(4)—C(5)—C(10)	120·0 (3)	C(2)—C(11)—C(16)	118·7 (2)			C(21)—C(22)—C(17)	120·4 (3)

(*c*) Torsion angles (°) (e.s.d.'s 0·5°)

S—C(3)—C(4)—C(5)	27·8	N—C(2)—C(11)—C(16)	−26·9	N—C(1)—C(17)—C(22)	180·7
S—C(3)—C(2)—C(11)	180·4	C(3)—C(2)—C(11)—C(12)	−30·2	C(2)—C(3)—C(4)—C(5)	205·8
S—C(1)—C(17)—C(18)	181·3	C(3)—C(2)—C(11)—C(16)	152·0	C(3)—C(4)—C(5)—C(6)	85·0
S—C(1)—C(17)—C(22)	1·7	N—C(1)—C(17)—C(18)	0·3	C(3)—C(4)—C(5)—C(10)	−92·5
N—C(2)—C(11)—C(12)	151·0				

(*d*) Most relevant intramolecular distances between non-bonded atoms (Å)

S· · ·C(22)	3·15 (1)	C(3)· · ·C(6)	3·30 (1)	N· · ·C(12)	3·70 (1)	N· · ·C(22)	3·72 (1)
S· · ·C(5)	3·06 (1)	C(3)· · ·C(12)	3·13 (1)	N· · ·C(16)	2·86 (1)	H(4)· · ·H(12)	2·22
S· · ·C(10)	3·41 (1)	C(3)· · ·C(16)	3·75 (1)	N· · ·C(18)	2·89 (1)	H(12· · ·C(4)	2·55
C(3)· · ·C(10)	3·38 (1)						

of the arrangement at C(1). A regular trigonal C atom is the unperturbed C(5) with all bond angles very close to 120·0°.

The C(2)–C(11) and C(1)–C(17) distances conform to the normal C(sp^2)–C(sp^2) bond length of 1·48 Å (Lide, 1962; Stoicheff, 1962; Bastiansen & Trætteberg, 1962) The C(3)–C(4), C(4)–C(5) and C(14)–C(23) bond lengths are close to the normal C(sp^2)–C(sp^3) single-bond value of 1·51 Å. The average bond lengths and angles in the phenyl rings are 1·389 (7) Å and 120·0 (3)°, respectively, and are within the expected range.

If we consider the characteristics of a selection of thiazole-type structures (Wheatley, 1961; Allmann, 1966, 1967; Newton, McDaniel, Baldwin & Paul, 1967; Smith, 1969; Fehlmann, 1970; Sténson, 1970; Miler Srenger, 1974; Sharma & Killean, 1974; Form, Raper & Downie, 1974; Killean, Lawrence, Cameron & Sharma, 1975) it can readily be seen that the endocyclic bond angles in the strained five-membered ring conform to the usual pattern (indicated in parentheses): C–S–C 90·4 (90·4), S–C–N 113·1 (112·7), C–N–C 112·4 (112·6), N–C–C 115·6 (113·9) and C–C–S 108·5° (110·3°). It is noticeable that the S–C–C bond angle is always smaller than the N–C–C angle. This aspect of the dissipation of strain is probably connected with non-bonded interactions and a consequence of the fact that S–C (3) is longer than N–C (2).

Inspection of the molecular configuration and bond lengths reveals that C(2)–C(3) and N–C(1) are both somewhat longer than normal double bonds: the C(2)–C(3) bond length of 1·379 Å is intermediate between the accepted C=C and C$\overset{\cdots}{-}$C values of 1·334 Å (Bartell & Bonham, 1957) and 1·394 Å (Sutton, 1965); on the other hand, a bond-valence value of 1·73 v.u. may be attributed to N–C(1) on the basis of the Lofthus (1959) scale. All other bonds of the thiazole ring are considerably shorter than normal single-bond distances and it is evident that there is (partial) π-electron delocalization. The N–C(2) distance of 1·380 Å (1·36 v.u.) is also significantly shorter than that of a C(sp^2)–N(sp^2) single bond (1·47 Å). Consideration of the covalent radii for S (Pauling, 1960) and trigonal C (Bastiansen & Trætteberg, 1962) leads one to expect values of 1·78 and 1·61 Å, respectively, for single and double S–C(sp^2) bonds. The estimate of the former value conforms to the findings (1·776 Å) in a phenylthiazolidinedione sodium salt (Matthews, 1964) and also compares well with the S–C(sp^2) single-bond length (1·83 Å) found in various thiazoles (Matthews, 1964; Mornon & Raveau, 1971; Amirthalingam & Muraldiharan, 1972; Mornon & Bally, 1972; Spek, 1972; Bally & Mornon, 1973). We conclude that there is considerable S–C double-bond character in (I) (as is found in other resonating structures). Typical S–C(sp^2) distances in thiazole compounds are 1·749 (8)–1·757 (8) Å (Sténson, 1970), 1·739 (3)–1·763 (3) Å (Fehlmann, 1970), 1·728 (3)–1·762 (3) Å (Smith, 1969); other such distances are listed by Sténson (1970) and Form *et al.* (1974). It should be noted that the two S–C bonds in (I) are essentially equal, at variance with the N–C bonds. Very similar observations with regard to the central-ring conformation can be made for the thiazole derivative which is structurally closest to (I) in that it carries substituents at the three C(sp^2) atoms, namely 4,4′-diacetoxy-5,5′-dimethyl-2,2′-bithiazolyl (Palmer, Wong & Lee, 1971).

Table 4. *Equations of the mean planes and displacements of atoms from these planes*

(*a*) Equations of best planes

The best planes, represented by the equation $lX + mY + nZ - p = 0$, are referred to the a^*, b', c orthogonal axis system with b' in the a^*b^* plane.

Plane	l	m	n	p	r.m.s. (Å)
Thiazole	0·4284	0·5055	0·7490	4·0615	0·010
Phenyl	0·4241	0·5283	0·7355	3·9658	0·010
Benzyl	−0·5166	−0·4243	0·7437	−3·3670	0·007
Tolyl	0·4579	0·8145	0·3562	3·6776	0·007

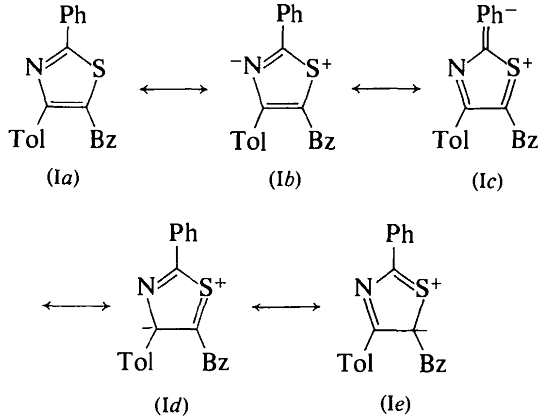
(*b*) Displacements (Å) of the atoms defining the best planes

Thiazole		Phenyl		Benzyl		Tolyl	
S	0·004	C(17)	0·012	C(5)	0·001	C(11)	−0·001
N	0·009	C(18)	−0·007	C(6)	0·002	C(12)	0·008
C(1)	−0·008	C(19)	−0·003	C(7)	−0·007	C(13)	−0·007
C(2)	−0·005	C(20)	0·009	C(8)	0·009	C(14)	0·001
C(3)	0·000	C(21)	−0·004	C(9)	−0·006	C(15)	0·005
		C(22)	−0·006	C(10)	0·000	C(16)	−0·005

The observations of the planarity and the bond-length considerations are all consistent with the existence of lone pairs of electrons on the N and S atoms and it is reasonable to expect that the transfer of charge from these lone-pair orbitals into a conjugated system involving double bonds greatly increases the stability of the molecule. It would appear that (I*a*) is the most important resonance hybrid in the planar part of the molecule with some minor dipolar contributions. The participation of each of the resonance forms can be expressed numerically by means of Pauling's (1960) equation

$$D_{\rm obs} = D_1 - (D_1 - D_2)\,\frac{1\cdot84\,(n+1)}{0\cdot84n + 0\cdot16}\,,$$

where D_1 and D_2 are taken as 1·47 and 1·27 Å for C–N and C=N, 1·79 and 1·61 Å for C–S and C=S$^+$, and 1·48 and 1·334 Å for C–C and C=C respectively. The following set of bond orders (n) can then be calculated: S–C(1) 1·12, S–C(3) 1·17, C(2)–C(3) 1·70, N–C(1) 1·70, and N–C(2) 1·36 v.u., where the latter conform to those derived according to Lofthus (1959). By solving the set of five equations with five unknown parameters it follows immediately that the main resonance forms are (I*a*) (I*c*) and (I*e*) in the approximate ratio of 0·65 : 0·20 : 0·15, with negligible contributions of (I*b*) and (I*d*).



The proposed resonance structures are in accordance with the fact that C(1)–C(17) is slightly shorter than C(2)–C(11). If the mesoionic compound is described in resonance terms (I*a*,*c*,*e*) then one might expect an intramolecular attraction between atoms bearing partial charges of opposite sign. The net result would enhance the decrease of the S–C(1)–C(17) bond angle with respect to N–C(1)–C(17). According to Julg's (1971) criterion for assessing relative degrees of π delocalization from bond-length data, modified by Wheeler & Ammon (1974), the aromaticity of the heterocyclic thiazole moiety in (I) is 0·90. Owing to the variety of atomic species in the heterocyclic ring, this value is likely to be overestimated.

The packing arrangement is illustrated in Fig. 3 which is a view down the normal to the heterocyclic ring of the reference molecule with coordinates x,y,z [A(000)]. The molecules, which are stacked so as to avoid overlap of the ring systems, are arranged in two sets of planes with a perpendicular separation of 4·06 Å [*cf.* $\bar{A}$(100)$\cdots A$(000)$\cdots A$(100)]. The large stacking distance is connected with the steric requirements of the S atoms and the out-of-plane rotations of the substituents to the central ring. The benzyl moieties are stacked at approximately 3·6 Å [*cf.* A(000) and $\bar{A}$(110)]. All the contacts between the molecules are of the van der Waals type and fall within the accepted range of values with no C$\cdots$C distance being shorter than 3·49 Å; the shortest intermolecular C$\cdots$S and C$\cdots$N contacts are 3·70 and 3·51 Å respectively (Table 5).

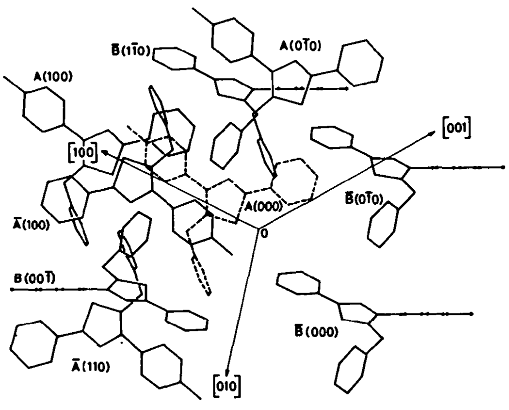


Fig. 3. Packing arrangement in 5-benzyl-2-phenyl-4-tolylthiazole projected onto the least-squares plane of molecule A(000). H atoms have been omitted. Relative heights (Å) in the direction of the projection are: 0 4·06; [100] 0·00; [010] −0·89; [001] −8·96. For notation see Table 5.

Table 5. *Intermolecular contacts* (Å) [*arbitrarily bounded at the sums of the van der Waals radii plus* 0·4 Å (*Pauling*, 1960, p. 260)]

The symbols A, $\bar{A}$, B and $\bar{B}$ denote molecules with coordinates x,y,z; $\bar{x},\bar{y},\bar{z}$; $x, \frac{1}{2}-y, \frac{1}{2}+z$; and $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$ respectively. In this notation $\bar{A}(\alpha\beta\gamma)$ stands for fractional coordinates $\alpha-x, \beta-y, \gamma-z$.

A(000)	$A(\bar{1}10)$	
C(8)	C(23)	3·97
C(9)	C(23)	3·94
A(000)	$A(0\bar{1}0)$	
N	C(7)	3·51
N	C(8)	3·60
C(1)	C(8)	3·97
A(000)	$\bar{B}(0\bar{1}0)$	
C(19)	C(22)	3·94
C(20)	C(22)	3·89
A(000)	$B(00\bar{1})$	
C(9)	C(19)	3·71
C(9)	C(20)	3·86
A(000)	A(010)	
C(7)	C(18)	3·91
C(8)	C(18)	3·84
A(000)	$\bar{B}(1\bar{1}0)$	
N	C(6)	3·58
C(15)	C(22)	3·81
A(000)	A(100)	
C(15)	C(21)	3·68
A(000)	$\bar{A}$(100)	
S	C(13)	3·70
C(2)	C(12)	3·58
C(2)	C(13)	3·77
A(000)	$\bar{A}$(100)	
C(3)	C(12)	3·64
C(3)	C(13)	3·49
C(4)	C(12)	3·94
C(4)	C(13)	3·88
C(11)	C(12)	3·80
C(12)	C(12)	3·57
A(000)	$\bar{B}$(100)	
S	C(15)	3·86
S	C(16)	3·87
C(6)	C(16).	3·94
C(6)	C(18)	3·94
C(7)	C(16)	3·99
C(12)	C(19)	3·90
C(13)	C(19)	4·00
A(000)	$\bar{A}$(110)	
C(4)	C(5)	3·78
C(4)	C(6)	3·72
C(4)	C(7)	3·82
C(4)	C(8)	3·98
C(4)	C(10)	3·93
C(5)	C(5)	3·57
C(5)	C(6)	3·80
C(6)	C(10)	3·98
C(8)	C(12)	3·74
C(8)	C(13)	3·89
A(000)	$\bar{B}$(000)	
S	C(20)	3·75
C(9)	C(21)	3·93

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Structure Cristalline et Moléculaire du Facteur S de la Virginiamycine

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Factor S, one of the two antibiotic components of virginiamycin, is a depsipeptide, $C_{43}H_{49}N_7O_{10}$, consisting of a hexapeptide chain cyclized by one lactone linkage. The structure of the solvate $S.3CH_3OH$ has been determined from 2524 independent reflexions collected on a diffractometer. The crystals are orthorhombic, space group $P2_12_12_1$ with $Z = 4$, $a = 20{\cdot}770$ (5), $b = 10{\cdot}441$ (3), $c = 22{\cdot}435$ (5) Å. The structure was solved by a version of *MULTAN*, modified to include statistical weighting, and has been refined by least-squares calculations to a final R of 0·090. The primary structure is consistent with that previously found by chemical methods [Vanderhaeghe & Parmentier (1959), *Bull. Soc. Chim. Belg.* **68**, 716–718]. The tertiary structure of the macrocycle is constrained by a transannular hydrogen bond.

Introduction

La virginiamycine est un antibiotique produit par un *Streptomyces* apparenté au *S. virginiae*. C'est un mélange de deux constituants majeurs, les facteurs M et S, possédant chacun des propriétés antibiotiques. Le premier est principalement actif à l'égard de *Micrococcus aureus*, le second de *Bacillus subtilis* (Crooy & De Neys, 1972). Le facteur M est une lactone macrocyclique de formule $C_{28}H_{35}N_3O_7$, dont la structure a été étudiée aux rayons X par Durant, Evrard, Declercq & Germain (1974).

La facteur S est un depsipeptide répondant à la formule $C_{43}H_{49}N_7O_{10}$. Vanderhaeghe & Parmentier (1959) en ont établi la structure primaire. Ces auteurs ont montré qu'il s'agit d'une chaîne hexapeptidique