Table 6. *Analysis of planarity of groups of atoms. The plane of best fit is defined by atoms with an asterisk. X, Y, Z are orthogonal coordinates in* Å

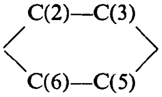
Transformation matrix from fractional to orthogonal coordinates

$$\begin{pmatrix} a\sin\gamma & 0 & -c\sin\alpha\cos\beta^* \\ a\cos\gamma & b & c\cos\alpha \\ 0 & 0 & c\sin\alpha\ \sin\beta^* \end{pmatrix}.$$

(1) Equation of the plane through C(2), C(3), C(5), C(6) of the pyridine ring

$$0\cdot1213X-0\cdot4355Y-0\cdot8920Z=-3\cdot2363\,.$$

	$\Delta.10^4$ (Å)	$\sigma.10^4$ (Å)
C(2)*	72	22
C(3)*	−74	22
C(5)*	138	32
C(6)*	−137	30
N(2)	202	21
C(4)	236	32

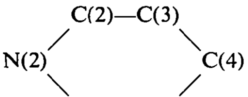


$\sum_4(\Delta/\sigma)^2=61\cdot48$

(2) Equation of the plane of the pyridine ring

$$0\cdot1221X-0\cdot4378Y-0\cdot8907Z=-3\cdot2383\,.$$

	$\Delta.10^4$ (Å)	$\sigma.10^4$ (Å)
N(2)*	102	21
C(2)*	8	22
C(3)*	−111	22
C(4)*	190	32
C(5)*	56	32
C(6)*	−246	30

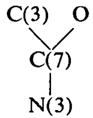


$\sum_6(\Delta/\sigma)^2=154\cdot74$

(3) Equation of the plane of the carbonyl carbon [C(7)]

$$0\cdot7690X+0\cdot2830Y-0\cdot5731Z=-0\cdot9805\,.$$

	$\Delta.10^4$ (Å)	$\sigma.10^4$ (Å)
C(3)*	−15	26
C(7)*	42	26
O*	−11	20
N(3)*	−17	25



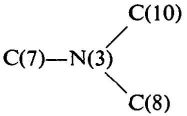
$\sum_4(\Delta/\sigma)^2=3\cdot71$

Table 6 (*cont.*)

(4) Equation of the plane of the amide nitrogen [N(3)]

$$0\cdot7285X+0\cdot4044Y-0\cdot5529Z=-0\cdot6640\,.$$

	$\Delta.10^4$ (Å)	$\sigma.10^4$ (Å)
C(7)*	−27	26
N(3)*	94	25
C(8)*	−28	31
C(10)*	−39	34



$\sum_4(\Delta/\sigma)^2=17\cdot35$

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The Crystal and Molecular Structure of 1,2-Benzisothiazol-3-yl Methyl Ketoxime

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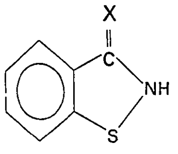
Crystals of 1,2-benzisothiazol-3-yl methyl ketoxime are orthorhombic, space group *Pbca*. The unit cell constants are $a=19\cdot613$ (8), $b=24\cdot192$ (9), $c=7\cdot550$ (3) Å, $Z=16$. The crystal structure has been determined by X-ray diffraction. Three-dimensional intensity data have been measured on a single-crystal automated diffractometer. The structure has been solved by direct methods and refined by least-squares methods (final $R=4\cdot3$ %). There are two independent molecules in the asymmetric unit. They are practically equal as far as distances, angles and configuration are concerned. The oxime group, =N–OH, is oriented *cis* with respect to the methyl group, *i.e.* the compound is the *anti*-1,2-benzisothiazol-3-yl methyl ketoxime. The whole molecule is nearly planar. Significant differences in bond distances and angles are found in the isothiazole ring of this compound and that of derivatives of 1,2-benzisothiazolin-3-one. The molecules are held together by a network of hydrogen bonds –OH···N, *i.e.* between the hydroxyl of the oxime group (OH) and the nitrogen atom of the isothiazole ring.

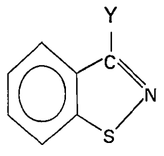
Introduction

1,2-Benzisothiazole derivatives form a class of compounds of pharmaceutical importance for their anaesthetic, antihistaminic and antifungal activities (Ponci, Vitali & Bertaccini, 1968; Vitali, Mossini, Bertaccini & Impicciatore, 1968; Vitali, Mossini, Mingiardi, Gaetani & Plazzi, 1971).

Two main types of compounds can be recognized by chemical methods: compounds (I), 1,2-benzisothiazolin-3-ylidene-X, where X = O, C(CN)CO_2Et, C(CN)$CONH_2$, *etc.* and compounds (II), 1,2-benzisothiazol-3-yl-Y, where Y = CH_3, C_2H_5, CH(CN)$CONH_2$, CH_2COOH, *etc.*



(I)



(II)

Several pairs of compounds, (I) and (II), are tautomers, being capable of transformation into each other by transposition of H.

In order to elucidate the structural parameters that characterize the two types, several structures have been investigated (Cavalca, Fava Gasparri, Mangia & Pelizzi, 1969; Cavalca, Gaetani, Mangia & Pelizzi, 1970; Corradi Bonamartini, Nardelli, Palmieri & Pelizzi, 1971; Corradi Bonamartini, Nardelli & Palmieri, 1972). Here are reported the results of the structure determination of one member of type (II), where $Y = C(CH_3)NOH$, 1,2-benzisothiazol-3-yl methyl ketoxime.

Experimental

Preparation

The compound was prepared by reaction of 1,2-benzisothiazol-3-yl methyl ketone with hydroxylamine hydrochloride (Amoretti, 1972). Crystals were obtained by slow cooling from an ethanol–water solution (m.p. 147–148 °C).

Crystal data

Compound: 1,2-benzisothiazol-3-yl methyl ketoxime $C_9H_8N_2OS$;

F.W. 192·23.

Unit cell (the parameters were determined from rotation and Weissenberg photographs and refined with data obtained on an automated single-crystal diffractometer, Cu $K\alpha$, $\bar{\lambda} = 1{\cdot}54178$ Å):

$a = 19{\cdot}613$ (8), $b = 24{\cdot}192$ (9), $c = 7{\cdot}550$ (3) Å; $V = 3582{\cdot}3$ Å^3; $Z = 16$; $D_x = 1{\cdot}433$ g cm^{-3}; μ(Cu $K\alpha$) = 27·93 cm^{-1}; $F(000) = 1600$; Space group: *Pbca* (D_{2h}^{15}, No. 61) from systematic absences.

Intensity data

The intensities were collected on a single-crystal automated diffractometer on line with a Siemens 304/*P* computer using Ni-filtered Cu $K\alpha$ radiation and the ω–2θ scan technique. A prismatic crystal of approximate dimensions 0·08 × 0·14 × 0·25 mm was aligned with its [001] axis along the φ axis of the diffractometer and all the reflexions with $2\theta \leq 140°$ were collected. In this way the intensities of 3388 independent reflexions were measured and 1977 were used in the crystal analysis, taking as unobserved the reflexions whose intensities were less than twice their standard deviations $\{\sigma^2(I) = [\text{total counts} + (0{\cdot}005I)^2]\}$. Corrections for Lorentz and polarization effects were made in the usual way. No correction for absorption was made. An absolute scale factor and the mean isotropic temperature factor were obtained by Wilson's (1942) method. The normalized structure factors, E_h, were then computed.

Table 1. *Final fractional atomic coordinates* ($\times 10^4$) *with e.s.d.'s*

	x	y	z
S(1)	3660 (1)	3494 (1)	4173 (1)
S(2)	4792 (1)	−1087 (1)	3229 (2)
O(11)	1339 (1)	2077 (1)	6937 (4)
O(21)	2572 (1)	491 (1)	892 (4)
N(11)	2888 (1)	3399 (1)	5036 (4)
N(12)	1976 (1)	2195 (1)	6191 (4)
N(21)	4005 (1)	−929 (1)	2539 (4)
N(22)	3228 (1)	330 (1)	1430 (4)
C(11)	3305 (2)	1911 (1)	4556 (5)
C(12)	3889 (2)	1667 (1)	3931 (6)
C(13)	4447 (2)	1974 (1)	3371 (5)
C(14)	4431 (2)	2546 (2)	3376 (5)
C(15)	3839 (2)	2798 (1)	3992 (5)
C(16)	3276 (1)	2498 (1)	4612 (4)
C(17)	2740 (2)	2868 (1)	5216 (5)
C(18)	2078 (2)	2718 (1)	6003 (5)
C(19)	1586 (2)	3164 (1)	6581 (6)
C(21)	4734 (2)	464 (1)	1826 (5)
C(22)	5396 (2)	649 (1)	2068 (5)
C(23)	5911 (2)	307 (1)	2762 (6)
C(24)	5772 (2)	−239 (1)	3210 (5)
C(25)	5107 (2)	−429 (1)	2924 (5)
C(26)	4584 (1)	−90 (1)	2271 (4)
C(27)	3955 (2)	−403 (1)	2106 (4)
C(28)	3285 (2)	−200 (1)	1527 (5)
C(29)	2730 (2)	−603 (1)	1098 (7)
H(11)	2906 (17)	1700 (13)	4882 (47)
H(12)	3933 (17)	1244 (14)	4024 (50)
H(13)	4848 (19)	1778 (14)	2907 (55)
H(14)	4833 (18)	2770 (14)	3193 (51)
H(15)	1652 (19)	3492 (15)	6081 (53)
H(16)	1115 (22)	3087 (17)	5926 (61)
H(17)	1396 (21)	3007 (16)	7744 (61)
H(18)	1368 (25)	1668 (19)	7031 (70)
H(21)	4357 (15)	717 (12)	1054 (43)
H(22)	5527 (15)	1058 (12)	1471 (42)
H(23)	6399 (16)	449 (13)	2962 (44)
H(24)	6157 (15)	−518 (12)	3758 (42)
H(25)	2846 (19)	−951 (15)	1375 (52)
H(26)	2500 (21)	−523 (16)	76 (57)
H(27)	2335 (23)	−429 (18)	2061 (64)
H(28)	2612 (27)	868 (20)	918 (71)

Structure determination and refinement

The structure was solved by means of the $\sum_2$ Sayre relationship in the symbolic addition procedure described by Germain & Woolfson (1968). Only 249 normalized structure factors greater than 1·89 were used in the phase determination. Reflexions 13,4,4 ($|E| = 3{\cdot}35$), 15,3,1 ($|E| = 2{\cdot}87$) and 312 ($|E| = 2{\cdot}78$) were chosen to define the origin. Symbols a, b, c and

d were assigned to the phases of reflexions 13,10,2 ($|E|=3{\cdot}38$), 9,24,2 ($|E|=4{\cdot}21$), 12,16,2 ($|E|=3{\cdot}37$) and 14,5,1 ($|E|=2{\cdot}76$) respectively. By applying the $\sum_2$ formula the solution obtained for the symbols was +, −, +, −. The signs of 242 reflexions were determined and used to compute an E map, which revealed the whole structure except for the hydrogen atoms. A structure-factor calculation using atomic parameters obtained from this E map gave an R value of 0·269. This value decreased to 0·13 after eight cycles of block-diagonal least-squares refinement with isotropic temperature factors. When anisotropic factors were introduced R dropped to 0·062 after six cycles. At this stage an (F_o-F_c) synthesis was computed and the positions of hydrogen atoms were found. The introduction of the hydrogen atoms in the subsequent refinements (with isotropic temperature factors) reduced the R value to 0·043 (observed reflexions only). Unit weights were used for the reflexions at every stage of the refinement.

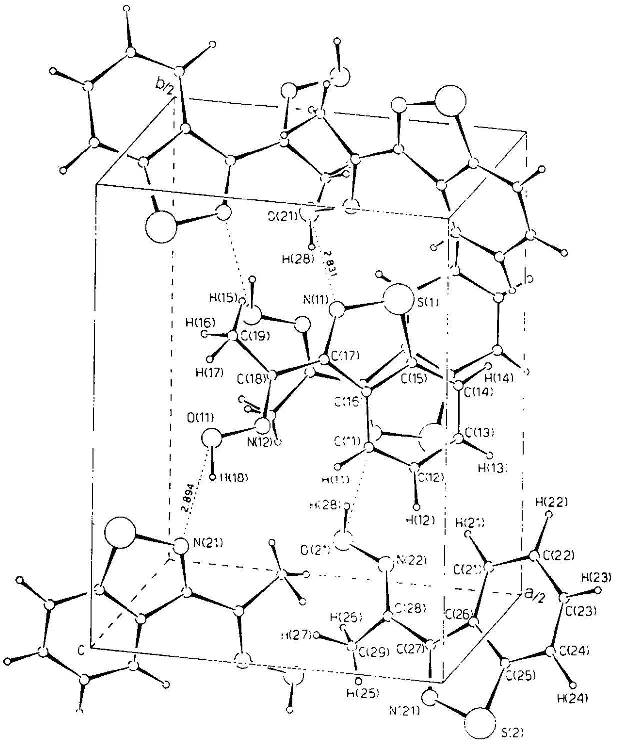


Fig. 1. Clinographic projection of the structure.

The final atomic coordinates are given in Table 1 and the thermal parameters in Table 2. A list of the observed and calculated structure factors is available as Supplementary Publication No. SUP 30019.*

The atomic scattering factors of Cromer & Mann (1968) were used for S, N, C, O and those of Stewart, Davidson & Simpson (1965) for H.

All the calculations were performed on the CDC 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna), using the programs written by Immirzi (1967).

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* This table has been deposited with the National Lending Library, England. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

The anisotropic temperature factors are in the form: $\exp\left[-0{\cdot}25(h^2a^{*2}B_{11}+\ldots 2klb^*c^*B_{23})\right]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(1)	4·485 (39)	2·491 (29)	5·022 (46)	−0·275 (30)	0·623 (40)	0·093 (34)
S(2)	3·530 (35)	2·733 (30)	6·591 (56)	0·334 (30)	−0·778 (42)	0·326 (38)
O(11)	4·261 (113)	3·713 (103)	8·272 (181)	−0·600 (93)	1·753 (129)	0·276 (118)
O(21)	2·868 (94)	3·325 (96)	9·283 (186)	0·241 (81)	−0·106 (122)	1·055 (121)
N(11)	4·083 (123)	2·233 (98)	4·850 (153)	0·210 (96)	0·035 (120)	0·016 (106)
N(12)	3·786 (125)	3·193 (112)	5·875 (171)	−0·175 (100)	0·136 (131)	−0·041 (120)
N(21)	3·482 (117)	2·436 (95)	5·269 (156)	−0·093 (92)	−0·422 (118)	0·076 (110)
N(22)	2·567 (104)	3·003 (105)	6·264 (178)	0·247 (93)	0·099 (116)	0·536 (119)
C(11)	4·491 (164)	2·358 (120)	4·641 (188)	0·159 (117)	−0·273 (145)	−0·075 (127)
C(12)	4·936 (178)	2·942 (137)	5·741 (220)	0·891 (124)	0·228 (173)	−0·076 (144)
C(13)	4·690 (174)	4·180 (157)	5·060 (207)	1·068 (141)	0·681 (167)	0·056 (159)
C(14)	4·119 (151)	3·972 (145)	4·907 (193)	0·243 (147)	0·467 (159)	−0·050 (149)
C(15)	4·152 (150)	2·516 (119)	3·685 (158)	0·070 (111)	0·094 (141)	0·059 (119)
C(16)	3·375 (126)	2·655 (108)	3·523 (152)	0·106 (121)	−0·430 (125)	−0·018 (118)
C(17)	3·698 (142)	2·378 (115)	3·647 (158)	−0·123 (106)	−0·308 (127)	0·189 (115)
C(18)	3·579 (142)	2·914 (124)	4·803 (184)	0·134 (112)	−0·554 (150)	−0·107 (134)
C(19)	4·566 (179)	3·402 (144)	8·372 (290)	0·880 (137)	1·784 (201)	0·419 (175)
C(21)	3·334 (132)	2·597 (118)	4·209 (167)	−0·240 (109)	0·644 (134)	−0·389 (124)
C(22)	3·600 (149)	3·256 (135)	5·475 (205)	−0·715 (117)	0·738 (153)	−1·044 (141)
C(23)	3·004 (134)	4·342 (156)	5·954 (217)	−0·390 (125)	0·218 (152)	−1·635 (162)
C(24)	2·829 (135)	4·509 (160)	5·372 (203)	0·253 (125)	−0·011 (147)	−0·937 (157)
C(25)	2·889 (130)	3·105 (128)	4·732 (190)	0·021 (108)	0·137 (134)	−0·814 (133)
C(26)	2·587 (119)	2·715 (115)	3·517 (154)	−0·023 (99)	0·381 (117)	−0·707 (115)
C(27)	3·051 (126)	2·255 (109)	4·087 (169)	−0·045 (101)	0·237 (126)	−0·248 (116)
C(28)	2·728 (126)	2·838 (120)	4·844 (186)	−0·184 (105)	0·035 (128)	0·067 (128)
C(29)	3·242 (155)	3·303 (147)	10·830 (336)	−0·794 (124)	−1·935 (194)	0·695 (190)

Table 2 (*cont.*)

Hydrogen atom parameters, *B*	
H(11)	5·53 (86)
H(12)	6·54 (97)
H(13)	7·40 (1·06)
H(14)	7·24 (1·04)
H(15)	7·77 (1·07)
H(16)	9·66 (1·29)
H(17)	9·47 (1·25)
H(18)	12·43 (1·61)
H(21)	4·73 (79)
H(22)	4·70 (77)
H(23)	5·14 (81)
H(24)	4·58 (77)
H(25)	7·62 (1·09)
H(26)	9·13 (1·21)
H(27)	11·00 (1·43)
H(28)	13·47 (1·75)

Description of the structure

The crystal structure of the compound is represented in Fig. 1. There are two independent molecules in the asymmetric unit, but they do not form a dimer; rather all the molecules of the structure are joined to one another by a network of hydrogen bonds between the oxime group =N–OH and the nitrogen atom of the benzisothiazole ring. Bond distances and angles in the two molecules are reported in Table 3.

Table 3. *Bond distances and angles in the two independent molecules*

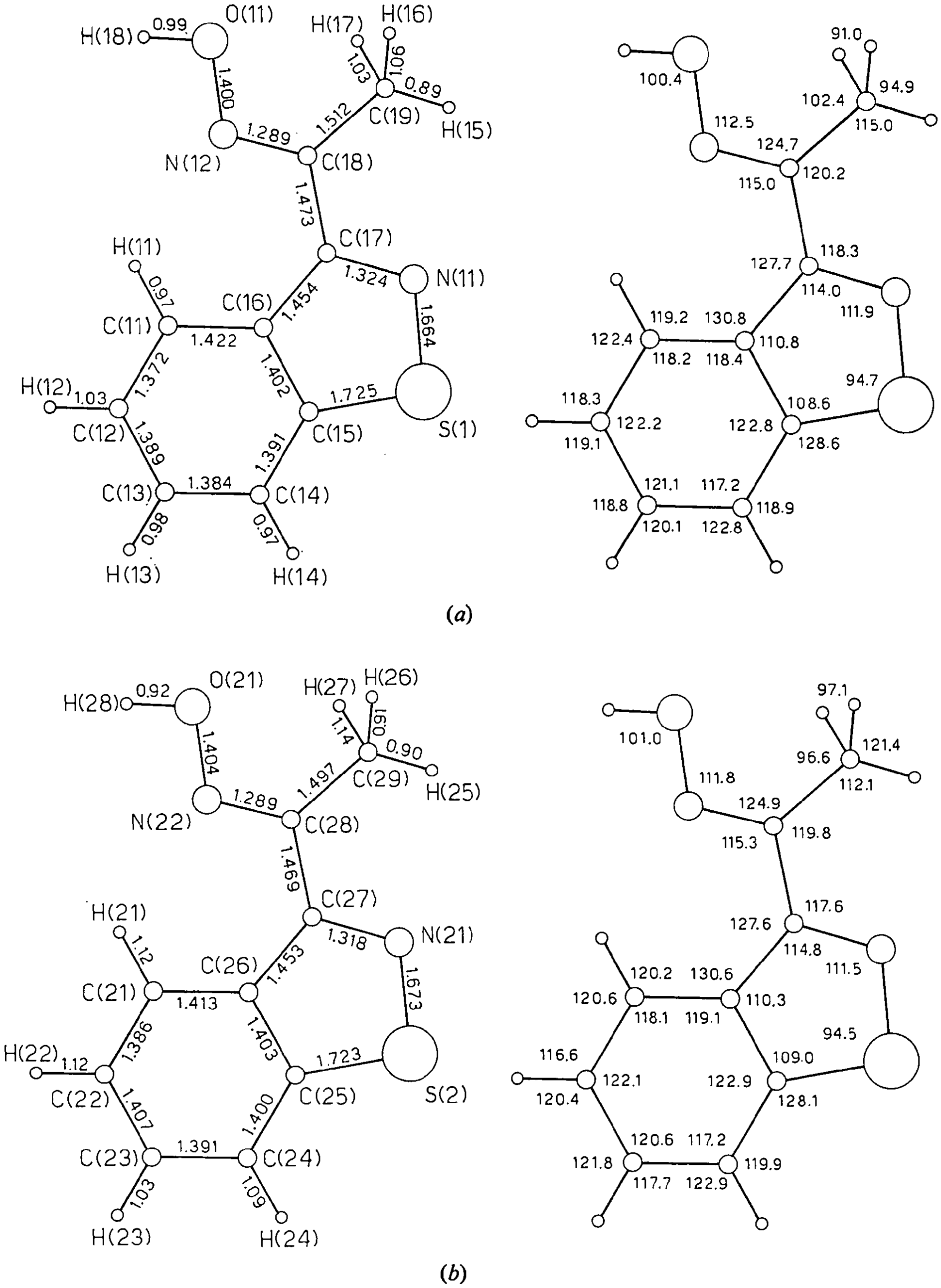
Distances			
C(15)–S(1)	1·725 (4) Å	C(25)–S(2)	1·723 (4) Å
N(11)–S(1)	1·664 (3)	N(21)–S(2)	1·673 (3)
N(11)–C(17)	1·324 (4)	N(21)–C(27)	1·318 (4)
C(17)–C(16)	1·454 (4)	C(27)–C(26)	1·453 (4)
C(16)–C(11)	1·422 (4)	C(26)–C(21)	1·413 (4)
C(11)–C(12)	1·372 (5)	C(21)–C(22)	1·386 (5)
C(12)–C(13)	1·389 (5)	C(22)–C(23)	1·407 (5)
C(13)–C(14)	1·384 (5)	C(23)–C(24)	1·391 (4)
C(14)–C(15)	1·391 (6)	C(24)–C(25)	1·400 (5)
C(15)–C(16)	1·402 (4)	C(25)–C(26)	1·403 (4)
C(17)–C(18)	1·473 (5)	C(27)–C(28)	1·469 (5)
C(18)–C(19)	1·512 (5)	C(28)–C(29)	1·497 (5)
C(18)–N(12)	1·289 (4)	C(28)–N(22)	1·289 (4)
N(12)–O(11)	1·400 (3)	N(22)–O(21)	1·404 (3)
C(11)–H(11)	0·97 (3)	C(21)–H(21)	1·12 (3)
C(12)–H(12)	1·03 (3)	C(22)–H(22)	1·12 (3)
C(13)–H(13)	0·98 (4)	C(23)–H(23)	1·03 (3)
C(14)–H(14)	0·97 (4)	C(24)–H(24)	1·09 (3)
C(19)–H(15)	0·89 (4)	C(29)–H(25)	0·90 (4)
C(19)–H(16)	1·06 (4)	C(29)–H(26)	0·91 (4)
C(19)–H(17)	1·03 (4)	C(29)–H(27)	1·14 (5)
O(11)–H(18)	0·99 (5)	O(21)–H(28)	0·92 (5)

Table 3 (*cont.*)

Angles			
C(15)–S(1)—N(11)	94·7 (2)°	C(25)–S(2)—N(21)	94·5 (2)°
S(1)—N(11)–C(17)	111·9 (2)	S(2)—N(21)–C(27)	111·5 (2)
N(11)–C(17)–C(16)	114·0 (3)	N(21)–C(27)–C(26)	114·8 (3)
C(17)–C(16)–C(15)	110·8 (2)	C(27)–C(26)–C(25)	110·3 (2)
C(16)–C(15)–S(1)	108·6 (2)	C(26)–C(25)–S(2)	109·0 (3)
C(16)–C(15)–C(14)	122·8 (3)	C(26)–C(25)–C(24)	122·9 (2)
C(15)–C(14)–C(13)	117·2 (4)	C(25)–C(24)–C(23)	117·2 (3)
C(14)–C(13)–C(12)	121·1 (3)	C(24)–C(23)–C(22)	120·6 (3)
C(13)–C(12)–C(11)	122·2 (2)	C(23)–C(22)–C(21)	122·1 (3)
C(12)–C(11)–C(16)	118·2 (3)	C(22)–C(21)–C(26)	118·1 (3)
C(11)–C(16)–C(15)	118·4 (3)	C(21)–C(26)–C(25)	119·1 (2)
C(16)–C(17)–C(18)	127·7 (2)	C(26)–C(27)–C(28)	127·6 (2)
N(11)–C(17)–C(18)	118·3 (3)	N(21)–C(27)–C(28)	117·6 (3)
C(17)–C(18)–C(19)	120·2 (2)	C(27)–C(28)–C(29)	119·8 (2)
C(19)–C(18)–N(12)	124·7 (3)	C(29)–C(28)–N(22)	124·9 (3)
C(17)–C(18)–N(12)	115·0 (3)	C(27)–C(28)–N(22)	115·3 (3)
C(18)–N(12)–O(11)	112·5 (3)	C(28)–N(22)–O(21)	111·8 (3)
C(11)–C(16)–C(17)	130·8 (3)	C(21)–C(26)–C(27)	130·6 (3)
C(14)–C(15)–S(1)	128·6 (3)	C(24)–C(25)–S(2)	128·1 (3)
H(11)–C(11)–C(16)	119·2 (19)	H(21)–C(21)–C(26)	120·2 (15)
H(11)–C(11)–C(12)	122·4 (19)	H(21)–C(21)–C(22)	120·6 (15)
H(12)–C(12)–C(11)	118·3 (19)	H(22)–C(22)–C(21)	116·6 (16)
H(12)–C(12)–C(13)	119·1 (19)	H(22)–C(22)–C(23)	120·4 (16)
H(13)–C(13)–C(12)	118·8 (20)	H(23)–C(23)–C(22)	121·8 (18)
H(13)–C(13)–C(14)	120·1 (21)	H(23)–C(23)–C(24)	117·7 (18)
H(14)–C(14)–C(13)	122·8 (21)	H(24)–C(24)–C(23)	122·9 (16)
H(14)–C(14)–C(15)	118·9 (21)	H(24)–C(24)–C(25)	119·9 (15)
C(18)–C(19)–H(15)	115·0 (25)	C(28)–C(29)–H(25)	112·1 (24)
C(18)–C(19)–H(16)	107·2 (23)	C(28)–C(29)–H(26)	113·8 (25)
C(18)–C(19)–H(17)	102·4 (22)	C(28)–C(29)–H(27)	96·6 (23)
H(15)–C(19)–H(16)	94·9 (34)	H(25)–C(29)–H(26)	121·4 (35)
H(15)–C(19)–H(17)	138·3 (34)	H(25)–C(29)–H(27)	111·7 (34)
H(16)–C(19)–H(17)	91·0 (34)	H(26)–C(29)–H(27)	97·1 (35)
N(12)–O(11)–H(18)	100·4 (29)	N(22)–O(21)–H(28)	101·0 (33)

The two independent molecular units (Fig. 2) do not differ significantly as regards distances, interatomic angles or configuration. In both molecules the =N–OH group is *cis* with respect to $-CH_3$, *i.e.* it is in *anti*-form with respect to the benzisothiazole ring. Very small differences, however, are apparent in deviations from complete planarity. In fact each of the two molecules as a whole does not depart much from the mean plane through the benzene or isothiazole ring, but the deviations in molecule 1 are less than those in molecule 2 (Table 4). There appears to be a fair degree of flexibility of the benzisothiazole skeleton, particularly in the 'folding as a book' of the two rings, benzene and isothiazole, as shown by the angles between normals, $\omega=1\cdot0^\circ$ for molecule 1 and $\omega=3\cdot0^\circ$ for molecule 2.

The benzene rings are not exactly regular. On purely statistical grounds (Hamilton, 1964) neither distances C–C = 1·372–1·422 Å for ring 1 and 1·386–1·413 Å for ring 2, nor angles C–C–C = 117·2–122·8° for ring 1 and 117·2–122·9° for ring 2 can be said to be equal within each ring; moreover the differences appear even more reliable because they are consistent in the two independent rings. Nevertheless it is hard to find reasons for these differences.



(*a*)

(*b*)

Fig. 2. Bond distances and angles in the two independent molecules.

Table 4. *Mean planes through benzene (A) and isothiazole (B) rings*

Equation of the plane is in the form: $m_1X+m_2Y+m_3Z=d$, where X, Y, Z are coordinates in Å.

	Molecule 1		Molecule 2	
	A	*B*	*A*	*B*
m_1	−0·3774	−0·3951	0·2374	0·2530
m_2	0·0029	−0·0049	−0·2838	−0·2355
m_3	−0·9260	−0·9186	−0·9290	−0·9384
d	−5·6228	−5·7726	0·6079	0·7105

	Δ Å × 10⁴	σ Å × 10⁴	Δ Å × 10⁴	σ Å × 10⁴		Δ Å × 10⁴	σ Å × 10⁴	Δ Å × 10⁴	σ Å × 10⁴
C(11)	43	38	287	38	C(21)	−34	37	808	37
C(12)	73	44	125	44	C(22)	80	37	1325	37
C(13)	−121	38	−352	38	C(23)	−43	44	912	44
C(14)	2	38	−331	38	C(24)	−84	37	159	37
C(15)	96	38	−45	38	C(25)	131	37	−32	37
C(16)	−93	29	54	29	C(26)	−51	29	67	29
C(17)	−322	38	−25	38	C(27)	328	30	−102	31
N(11)	−122	29	13	29	N(21)	1134	29	75	29
S(1)	204	10	4	10	S(2)	1043	16	−8	16
Interplanar angle		$\omega_{AB}=1\cdot0°$					$\omega_{AB}=3\cdot0°$		

The two isothiazole rings are equal and planar. The mean bond lengths (Table 5) of C(6)–C(7), C(7)–N(1), N(1)–S, S–C(5) are shorter than the corresponding single-bond distances, so that a certain amount of aromatic character can be assigned to them. The distances and angles in the isothiazole ring can be compared with values obtained in compounds of type (I) (Cavalca *et al.*, 1969; Cavalca *et al.*, 1970). In compounds of type (I), the angle C(5)–S–N(1) has $\bar{\alpha}_I=$ 90·2 (2)° against $\bar{\alpha}_{II}=94\cdot6$ (1)° and for S–N(1)–C(7), $\bar{\alpha}_I=116\cdot1$ (2)° against $\bar{\alpha}_{II}=111\cdot7$ (1)°, for C(5)–C(6)–C(7), $\bar{\alpha}_I=111\cdot6$ (3)° against $\bar{\alpha}_{II}=110\cdot6$ (1)°, for N(1)–C(7)–C(6), $\bar{\alpha}_I=109\cdot5$ (3)° against $\bar{\alpha}_{II}=114\cdot4$ (2)°, for C(6)–C(5)–S, $\bar{\alpha}_I=112\cdot3$ (2)° against $\bar{\alpha}_{II}=108\cdot7$ (2)°. The distances also confirm that the pentatomic ring changes from one type to the other; the differences in the bond lengths are consistent with an increase of the single-bond character in the ring type (I) with respect to the ring type (II); this is true not only for C(7)–N(1) but also for other bonds, N(1)–S, C(5)–S, C(6)–C(7). Incidentally it is noticeable that the differences in the benzene portion of type (I) and type (II) are much smaller than the differences in the isothiazole ring, as would be expected because of the outstanding aromatic character of the benzene ring.

The changes in the isothiazole ring offer a clue to the interpretation of the reactivity of these compounds. In fact compounds (I) rather than compounds (II) are assumed to undergo some transformations (Böshagen, Feltkamp & Geiger, 1967; Vitali *et al.*, 1971) implying rotation around C(6)–C(7):

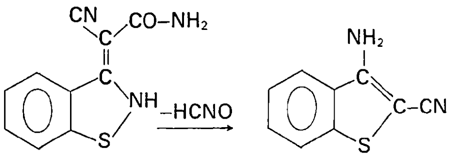


Table 5. *Comparison of bond distances and angles in benzisothiazole molecules of type* I *and* II

Ring	Bond	Type II* $\bar{d}_{II}$	Type I† $\bar{d}_I$	$(\bar{d}_I-\bar{d}_{II})\times10^3$
Isothiazole	C(5)–S	1·724 (3) Å	1·740 (3) Å	16
	N(1)–S	1·668 (2)	1·703 (3)	35
	N(1)–C(7)	1·321 (3)	1·353 (7)	32
	C(7)–C(6)	1·454 (3)	1·477 (7)	23
	C(5)–C(6)	1·403 (3)	1·387 (7)	−16
Benzene	C(4)–C(5)	1·396 (4)	1·413 (7)	17
	C(3)–C(4)	1·388 (3)	1·380 (7)	−8
	C(2)–C(3)	1·398 (4)	1·410 (7)	12
	C(1)–C(2)	1·379 (4)	1·380 (7)	1
	C(6)–C(1)	1·418 (3)	1·393 (7)	−25
	C(5)–C(6)	1·403 (3)	1·387 (7)	−16

Ring	Angle	$\bar{\alpha}_{II}$	$\bar{\alpha}_I$	$\bar{\alpha}_I-\bar{\alpha}_{II}$
Isothiazole	C(5)–S——N(1)	94·6 (1)°	90·2 (1)°	−4·4
	C(6)–C(5)–S	108·8 (2)	112·3 (2)	+3·5
	S——N(1)–C(7)	111·7 (1)	116·1 (2)	+4·4
	N(1)–C(7)–C(6)	114·4 (2)	109·5 (3)	−4·9
	C(5)–C(6)–C(7)	110·6 (1)	111·6 (3)	+1·0
Benzene	C(6)–C(5)–C(4)	122·9 (2)	120·5 (3)	−2·4
	C(5)–C(4)–C(3)	117·2 (2)	117·6 (3)	+0·4
	C(4)–C(3)–C(2)	120·9 (2)	121·7 (3)	+0·8
	C(3)–C(2)–C(1)	122·2 (2)	120·3 (3)	−1·9
	C(2)–C(1)–C(6)	118·2 (2)	118·5 (3)	+0·3
	C(1)–C(6)–C(5)	118·8 (2)	121·4 (3)	+2·6

* Present work.

† Cavalca, Fava Gasparri, Mangia & Pelizzi (1969); Cavalca, Gaetani, Mangia & Pelizzi (1970).

This rotation should be favoured by the increased tetrahedral character of C(7) and by the single-bond character of C(6)–C(7). On the contrary, compounds of type (II) with the angle at C(7) nearer to 120° are more stable.

The angles around C(17), C(18), C(27), C(28) show that the bonds radiating from them are planar; they can be assigned an sp^2 configuration.

The bonds C(17)–C(18) = 1·473 (5) and C(27)–C(28) = 1·469 (5) Å are only slightly shorter than the expected

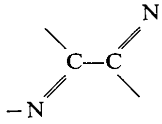
Table 6. *Hydrogen bonds*

O(11)–H(18)···N(21^{i})	2·894 (4) Å	O(11)–H(18)–N(21^{i})	153·7 (4·2)°
H(18)···N(21^{i})	1·97 (5)	H(18)–O(11)–N(21^{i})	17·5 (2·8)
O(21)–H(28)···N(11^{ii})	2·831 (4)	O(21)–H(28)–N(11^{ii})	155·9 (4·8)
H(28)···N(11^{ii})	1·97 (5)	H(28)–O(21)–N(11^{ii})	16·5 (3·3)

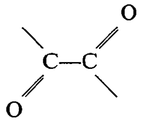
Asymmetric units

i	$\frac{1}{2}-x,\ -y,\ \frac{1}{2}+z$
ii	$x,\ \frac{1}{2}-y,\ -\frac{1}{2}+z$

value C_{sp2}–C_{sp2} = 1·49 Å. The system (*A*) can be compared with system (*B*) of oxalates (Sequeira, Srikanta & Chidambaram, 1970) and amidoxalates (Braibanti, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1971 and references therein; Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1972). The system (*A*), however, does not possess the lengthened C_{sp2}–C_{sp2} bond found in system (*B*). The bonds C(18)–C(19) = 1·512 (5) and C(28)–C(29) = 1·497 (5) Å are in agreement with values expected for similar bonds in amides, *i.e.* for C_{sp2}–C_{sp2} bonds.



(*A*)



(*B*)

The bond lengths C(18)–N(12) = 1·289 (4) and C(28)–N(22) = 1·289 (4) Å of the ketoxime groups suggest pronounced π-contribution in those bonds, whereas the bond lengths N(12)–O(11) = 1·400 (3) and N(22)–O(21) = 1·404 (3) Å are pure σ-bonds.

The angles involving hydrogen atoms around the benzene carbon atoms are satisfactorily close to 120°, but the angles of the methyl groups show departures from the tetrahedral values.

The intermolecular hydrogen bonds (Table 6) between the oxime residue and the nitrogen atom of the isothiazole ring [2·894 (4) and 2·831 (4) Å] are fairly strong. The hydrogen atoms are nearly 17° out of the line joining the oxygen atoms to the nitrogen atoms.

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