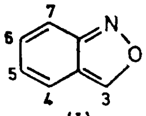
Crystal and Molecular Structure of 5-Chloro-2,1-benzisothiazole

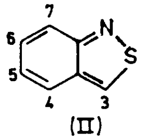
By **M. Davis** and **M. F. Mackay**, Department of Chemistry, La Trobe University, Bundoora, Victoria, Australia 3083
W. A. Denne,* Division of Chemical Physics, CSIRO, P.O. Box 160, Clayton, Victoria, Australia 3168

The crystal and molecular structure of the title compound has been determined by *X*-ray crystallographic analysis from diffractometer data. The crystals belong to the orthorhombic space group $P2_12_12_1$, with a = 3·926, b = 9·928, c = 18·204 Å and Z = 4. The structure was solved by the heavy-atom method, and refined by Fourier and least-squares procedures to a final R of 0·035 with 475 observed terms. The molecule is planar to within ±0·014 Å, and the C–S and N–S bond lengths are 1·664 ± 0·005 and 1·636 ± 0·005 Å respectively. These dimensions and others indicate considerable π electron delocalization extending throughout the two fused rings. N.m.r. evidence is also reported.

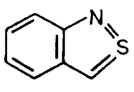
THE bonding in 2,1-benzisothiazole and related compounds has been the subject of some debate.[1,2] By analogy with the *X*-ray structure of a 2,1-benzisoxazole (I) derivative,[3] the state of bonding in the thiazole molecule may be presumed to be best represented by (II). The thiazole, however, differs from the oxazole in many of its chemical reactions, and in particular shows little or none of the '*ortho*-quinonoid' reactivity that might be expected of (II).[1] It has therefore been suggested that (III) is a major resonance contributor.



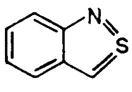
(I)



(II)



(III)



(IV)

In an attempt to clarify this situation, an *X*-ray analysis of 5-chloro-2,1-benzisothiazole (m.p. 72 °C) was undertaken to establish accurate dimensions in this molecule and hence to indicate the bonding in 2,1-benzisothiazoles.

EXPERIMENTAL

Crystal Data.—C_7H_5ClNS, $M = 170{\cdot}63$, Orthorhombic, $a = 3{\cdot}926 \pm 0{\cdot}002$, $b = 9{\cdot}928 \pm 0{\cdot}002$, $c = 18{\cdot}204 \pm 0{\cdot}004$ Å, $U = 709{\cdot}5$ Å^3, $D_m = 1{\cdot}586 \pm 0{\cdot}004$ (by flotation), $Z = 4$, $D_c = 1{\cdot}584$, $F(000) = 348$. Space group $P2_12_12_1$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) 67·2 cm^{-1}.

Unit cell parameters were determined from diffractometer settings. A complete set of non-equivalent intensities to 0·85 Å was recorded with Cu-K_α radiation on a Picker automatic diffractometer, from a crystal of dimensions 0·074 × 0·254 × 0·415 mm. Intensity measurements were recorded for 661 terms of which 481 had values significantly above background. Corrections were made for absorption[4] but not for extinction, although the six strongest terms which, by comparison with $|F_c|$ values, appeared to be significantly affected, were omitted from the final refinement cycles. All scattering factors used in the analysis were taken from ref. 5.

The structure was solved by the heavy-atom method. The sulphur and chlorine atom sites were derived from an 'unsharpened' three-dimensional Patterson synthesis. A subsequent Fourier map phased on the sulphur and chlorine contributions to the structure factor, revealed the sites of the carbon and nitrogen atoms. After least-squares refinement † of the located atoms with individual isotropic temperature factors, R was 0·098. The hydrogen atom sites were then derived from a difference Fourier, and refinement of all atoms, with anisotropic temperature factors for all but hydrogen, reduced R to 0·062. At this stage, the standard deviations for the carbon atoms were still quite high (0·012 Å) and two of the benzene ring bond lengths were far from typical [C(3a)–C(7a) 1·464, and C(6)–C(7) 1·310 Å]. Inspection of the data revealed that about 20% of $\Sigma||F_o| - |F_c||^2$ was attributable to the largest observed term, F_{020} ($|F_o|$ for this term was appreciably $< |F_c|$), and its omission in the refinement reduced R to 0·046. Although the general fit of $|F_o|$ with $|F_c|$ was thereby improved considerably, that of the remaining large structure amplitudes had worsened significantly again in the direction consistent with the presence of extinction. On the assumption that these discrepancies were caused by extinction, the next five large terms were also omitted and further refinement was indicated by the reduction of R to 0·035. There were now no exceptionally large variations between the $|F_o|$ and $|F_c|$ terms, the C(3a)–C(7a) and C(6)–C(7) bonds were now 1·419 and 1·341 Å respectively, and the benzene ring C–H bonds did not differ significantly from the expected value of 1·01 Å.[6] In the final refinements, the hydrogen atoms were given the same anisotropic thermal parameters as the heavy atoms to which they were attached.

The final atomic parameters together with their estimated standard deviations are given in Table 1, while bond lengths, bond angles, and deviations of the atoms from the mean molecular plane are shown in Figure 1. Libration corrections were estimated and were found to be insignificant in comparison with the precision of this analysis. A line diagram of the structure projected down the *a* axis is given in Figure 2 which also includes some short intermolecular approach distances. Observed and calculated

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† All least-squares refinements were carried out using the Busing and Levy programme ORFLS, with unit weight being given to all terms.

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[2] W. G. Salmond, *Quart. Rev.*, 1968, **22**, 253.

[3] M. Sundaralingam and G. A. Jeffrey, *Acta Cryst.*, 1962, **15**, 1035.

[4] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1959, **10**, 180.

[5] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[6] B. Dawson, personal communication.

TABLE 1

Final atomic co-ordinates and thermal parameters (all × 10^4) * with estimated standard deviations in parentheses

	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(3)	−0074(16)	1974(5)	6912(3)	745(60)	87(6)	40(2)	44(16)	4(10)	0(3)
C(3a)	0328(15)	1093(5)	6334(3)	485(45)	68(5)	31(2)	1(15)	19(7)	1(3)
C(4)	−0565(14)	1236(5)	5581(3)	580(44)	74(5)	36(2)	8(17)	14(8)	4(3)
C(5)	0172(14)	0200(5)	5130(3)	509(48)	98(6)	33(2)	−27(17)	−1(8)	−3(3)
C(6)	1775(17)	−0989(5)	5375(3)	549(51)	80(6)	46(2)	−17(17)	16(10)	−10(3)
C(7)	2514(16)	−1153(5)	6083(3)	685(54)	59(5)	48(2)	54(16)	13(9)	1(7)
C(7a)	1902(15)	−0107(5)	6587(3)	522(45)	80(6)	36(2)	−30(17)	−3(8)	15(3)
N	2725(14)	−0146(5)	7312(2)	831(44)	123(6)	36(1)	1(15)	2(8)	16(3)
S	1441(5)	1272(2)	7675(1)	955(15)	141(2)	31(1)	−39(6)	9(2)	0(1)
Cl	−0940(5)	0317(2)	4205(1)	919(15)	173(2)	34(1)	7(6)	−20(2)	−10(1)
H(3) †	−1108(128)	2669(41)	6868(23)						
H(4) †	−1706(120)	2055(38)	5441(21)						
H(6) †	2061(123)	−1758(39)	5027(21)						
H(7) †	3867(134)	−1876(40)	6242(20)						

* The expression used for the temperature factor was $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. † These atoms were given the same β_{ij} values as the heavier atoms to which they were attached.

structure factors are listed in Supplementary Publication No. SUP 20297 (7 pp., 1 microfiche).*

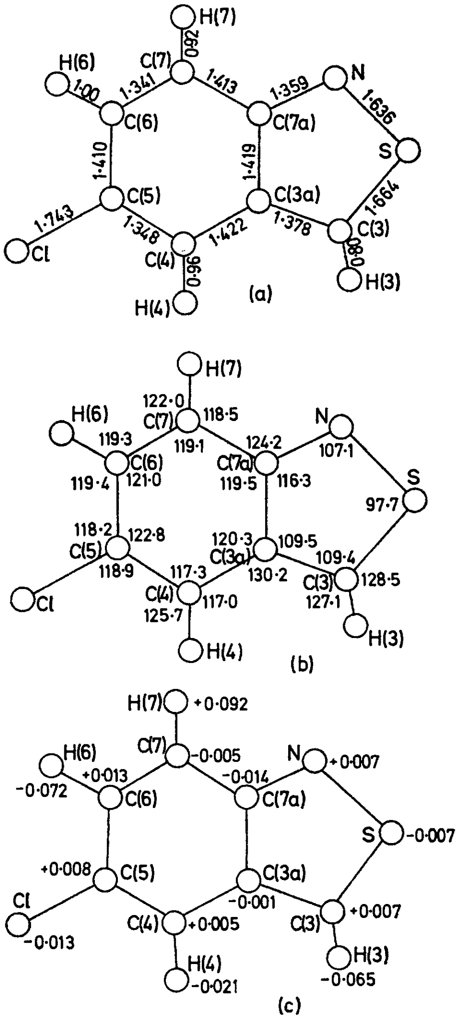

FIGURE 1 (a) Bond lengths; estimated standard deviations for lengths involving Cl and S 0·005 Å, for those involving H 0·04 Å, and for all others 0·007 Å. (b) Bond angles; estimated standard deviations for all angles involving H 3°, and for all others 0·3°. (c) Deviations of the atoms from the mean molecular plane; estimated standard deviations for all atoms 0·005 Å, except for S and Cl 0·002 Å

DISCUSSION

The molecule is planar within experimental error with the plane equation: $0{\cdot}8995X + 0{\cdot}4015Y - 0{\cdot}1918Z + 1{\cdot}6598 = 0$ (the hydrogen atoms were not included in the calculation) and the distances of individual atoms from the plane are given in Figure 1(c). The mean deviation of the hydrogen atoms from the molecular plane is ±0·06 Å and of all other atoms ±0·008 Å, both of which are comparable with the respective estimated standard deviations in the positional parameters.

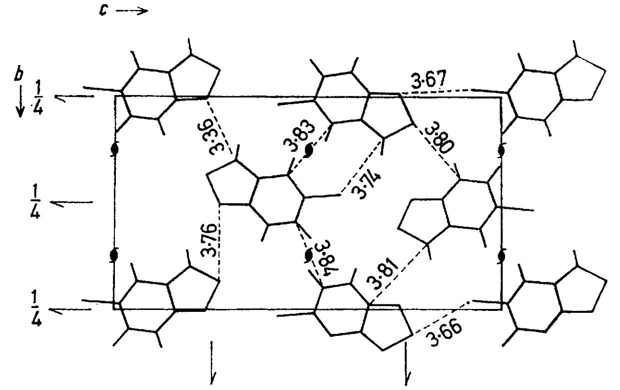

FIGURE 2 Line diagram of the structure viewed down the *a* axis

Bond lengths in the benzene ring are approximately symmetrical about the line extending between the mid-points of the C(5)–C(6) and C(3a)–C(7a) bonds [see Figure 1(a)]. The mean C–C bond in the benzene ring is 1·392 Å, but bonds C(4)–C(5) and C(6)–C(7) are 1·348 and 1·341 Å, considerably less than the standard value of 1·395 Å,[7] whereas C(3a)–C(4), C(5)–C(6), C(7)–C(7a), and C(3a)–C(7a) have larger values of 1·422, 1·410, 1·413, and 1·419 Å. Thus there is apparent bond fixation in the benzene ring. Bonds C(4)–C(5) and C(6)–C(7) have considerable double-bond character while the others have a larger component of single-bond

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[7] *Chem. Soc. Special Publ.*, No. 11, 1956; No. 18, 1965.

character. Indication of similar bond-fixation, but to a somewhat lesser degree, has been noted in naphthalene[8] [see Figure 3(b)], where the corresponding extreme bond lengths are 1·361 and 1·425 Å respectively. The C(5)–Cl bond of 1·743 Å is typical of reported values for such bonds.[9]

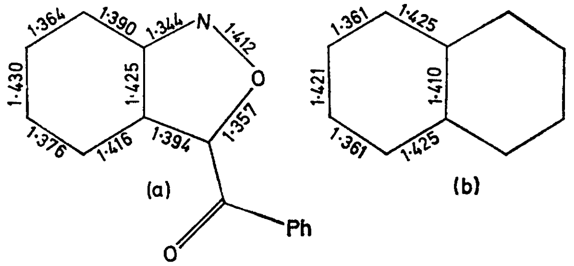

FIGURE 3 Bond lengths in two related structures. (a) Benzoylbenzisoxazole; estimated standard deviations 0·008 Å. (b) Naphthalene; estimated standard deviations 0·005 Å

In the thiazole ring, the C(7a)–N bond (1·359 Å) is much less than the essentially single C(aromatic)–N bond (1·413 Å) in *N*-acetanilide[10] and the mean of 1·468 Å in *s*-triaminobenzene;[11] the C(3)–C(3a) bond (1·378 Å) is close to the standard aromatic C–C bond (1·395 Å) and is certainly significantly different from the standard values of 1·335 and 1·537 Å for double and single C–C bonds respectively.[7] The two bonds involving sulphur must also have considerable double-bond character, as the C(3)–S bond of 1·664 Å lies approximately midway between the expected single-bond value[12] of 1·812 Å and the spectroscopic double-bond value[13] of 1·554 Å found in carbon disulphide; the value of the N–S bond (1·636 Å) also lies approximately midway between the single- and double-bond values of 1·74 and 1·56 Å respectively obtained from summing the Pauling[14] single- and double-bond covalent radii. The N–S–C(3) angle (97·7°) is in agreement with other reported values,[15] but as expected its value is much lower than that of the N–O–C angle (110·5°) in 3-benzoyl-2,1-benzisoxazole.[3] The lower values for angles X–S–X compared with the values for X–O–X has been explained by assuming participation of *d* orbitals in the bonding.[16]

TABLE 2

Comparison of n.m.r. parameters for (II) with those for (I). Spectra obtained at 60 MHz of samples containing tetramethylsilane, without solvent

	δ/p.p.m.			*J*/Hz			*J*/Hz	
H atom	(II)	(I)	Coupled H atoms	(II)	(I)	Coupled H atoms	(II)	(I)
3	9·06	9·08	3,4	0·38	−0·12	4,6	1·23	0·95
4	7·63	7·46	3,5	0·18	−0·10	4,7	0·85	1·18
5	7·09	6·90	3,6	0·17	−0·04	5,6	6·02	6·40
6	7·31	7·19	3,7	0·94	1·08	5,7	1·21	0·69
7	7·78	7·53	4,5	7·92	8·84	6,7	8·40	9·05

In the crystal structure, the molecules pack with their molecular planes inclined at *ca.* 26° to (100). No intermolecular contacts are significantly less than those anticipated from van der Waals radii. The closest molecular approaches are: N ··· C(1) 3·335, Cl ··· C(1) 3·742, Cl ··· N 3·674, and Cl ··· S 3·656 Å (see also Figure 2).

In view of the molecular planarity and dimensions, the molecule is perhaps well described as a system in which there is considerable π-electron delocalization extending throughout the two fused rings as in naphthalene. This can be correlated with the lack of '*ortho*-quinonoid' reactivity. A reasonable model for the state of bonding in 2,1-benzisothiazole is therefore provided by a resonance hybrid of approximately equal contributions from (II), (III), and (IV). The benzisoxazole bond lengths given in 3-benzoyl-2,1-benzisoxazole [see Figure 3(a)] show the N–O bond to be definitely single and hence in this case delocalization is not complete. This no doubts accounts for the differences in chemical reactivity.

The n.m.r. parameters for 2,1-benzisothiazole[17] and for 2,1-benzisoxazole[18] (Table 2) provide some additional evidence of bond fixation in the benzenoid ring of this type of heterocyclic compound. Use of the empirical relationship[19,20] between the *ortho*-coupling constant of hydrogen atoms on adjacent sp^2 hybridized carbon atoms, and the π bond-order of that particular carbon–carbon bond, *i.e.* J *ca.* $11{\cdot}75p - 0{\cdot}23$, affords values for the π bond-orders in the two parent members of these

TABLE 3

π-Bond orders calculated for n.m.r. coupling constants using the equation ref. 20

Bond	2,1-Benzisothiazole	2,1-Benzisoxazole
C(4)–C(5)	0·694	0·772
C(5)–C(6)	0·532	0·564
C(6)–C(7)	0·736	0·790

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heterocyclic systems (Table 3). There is greater π bond-order in the C(4)–C(5) and C(6)–C(7) bonds, indicative of some degree of bond fixation. This fixation is greater in 2,1-benzisoxazole, in accord with the greater reactivity of this compound. Although one cannot directly compare 2,1-benzisothiazole with its 5-chloro-derivative, it would be surprising if the chlorine atom in the latter grossly perturbs the benzenoid ring. Bond lengths and π bond-orders are inversely related, and thus the n.m.r. results seem to confirm the structural data.

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