

The Crystal Structure of Phenylthiazolidinedione

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Crystals of phenylthiazolidinedione are monoclinic with space group $P2_1/a$; the unit-cell dimensions are

$$a = 9.620, b = 6.751, c = 14.758 \text{ \AA}; \beta = 102^\circ 6'$$

The crystal structure was solved by a partial interpretation of the three-dimensional Patterson function, followed by the application of Woolfson's (1956) improved 'heavy atom' technique. The structural parameters of the heavy atoms, including anisotropic temperature factors, were refined by the method of 'differential difference' syntheses; the positions of the hydrogen atoms were found geometrically, and then refined. The final R index for the 1137 observed reflexions was 6.9%.

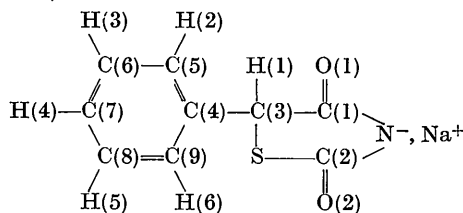
The thiazolidine ring is significantly aplanar, C(3) being 0.134 Å from the best plane through the remaining four ring atoms.

Introduction

Phenylthiazolidinedione (PTD) has a structural similarity to many of the antiepileptiform drugs in current use (*e.g.* phenobarbitone, dilantin, mesantoin and epidon). Its pharmacological properties have been investigated by Shulman (1957), who found that PTD and related substances may have a use in the treatment of epileptiform seizures. This analysis of the crystal structure of PTD was undertaken firstly because of the biochemical interest, and secondly to determine the dimensions of the unstrained thiazolidine ring. (Since this work was commenced, the crystal structures of rhodanine (van der Helm, Lessor & Merritt, 1962), merocyanine (Germain, Piret, van Meersche & de Kerf, 1962) and thiamine hydrochloride (Kraut & Reed, 1962) have been published; these compounds all contain a thiazole ring, but with widely different substituents in each case.)

A sample of the sodium salt of PTD (Na PTD) was kindly donated by Nicholas (Aust.) Pty Ltd.

The structural formula, showing the atom numbering used, is



Experimental

Unit cell and space group

Crystals were grown from water, the saturated solution being kept in a constant-temperature room

for several weeks. The crystals always occurred as thin, irregular plates, formed parallel to (001) and often twinned on this plane. Cleavage parallel to (001) was most marked, and the crystal plates could also be split parallel to [010] in approximately the (100) plane.

The crystal selected for rotation about the b axis measured 0.08×0.05 mm in cross section. Attempts to cut or cleave crystals suitable for rotation about other axes invariably resulted in multiple cleavage parallel to (001); it was therefore decided to use the b -axis crystal for all accurate intensity measurements. Absorption effects were ignored, the difference between the maximum and minimum corrections to the F_o 's being only 4.5%. The different layers of b -axis data were brought to an approximately common scale by comparison with $0kl$ spectra recorded from a somewhat imperfect crystal rotated about its a axis.

From systematic absences on Weissenberg photographs, the space group was established unequivocally as $P2_1/a$. The lattice constants were determined by the back-reflexion extrapolation method of Farquhar & Lipson (1946), and are summarized in Table 1. Assuming four molecules in the unit cell, the expected density was 1.537 g.cm^{-3} ; the value observed by flotation was 1.53 g.cm^{-3} .

Table 1. Lattice constants and their standard deviations

$a \sin \beta = 9.4064 \pm 0.0012 \text{ \AA}$	$a = 9.620 \pm 0.002 \text{ \AA}$
$c \sin \beta = 14.4302 \pm 0.0021$	$c = 14.758 \pm 0.003$
$\beta = 102^\circ 6.2' \pm 0.8'$	$b = 6.751 \pm 0.002$

Collection of intensity data

The intensity data for the layers $h0l$ through $h5l$ were recorded by equi-inclination Weissenberg photographs taken with nickel-filtered $\text{Cu } K\alpha$ radiation. The reflexions were integrated by the use of a

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mechanism attached to the film cassette, and the multiple film technique used to bring the reflexion densities within the linear density-intensity region. Those reflexions of sufficient intensity were measured photometrically (Gurr (1963) discusses the method in more detail). The weaker intensities were estimated from a second set of non-integrated photographs by the method of eye estimation (in both cases, exposure times of about 100 hr were used for each layer). The photometered and eye-estimated intensities were brought to a common scale by comparing reflexions whose intensities were measurable by both methods. All the intensities used are the average of at least two measurements made at different times.

Within the limiting sphere for copper radiation, there are 2107 independent reflexions. Of the 1743 theoretically observable in the layers $h0l$ through $h5l$, 1137 were observed to have a non-zero intensity, and approximately half of these had sufficient intensity to be photometered.

Determination of the structure

After an unsuccessful attempt using projections, the correct structure was determined from a partial interpretation of the three-dimensional Patterson function. Before this calculation, the method of Wilson (1942) was used to bring the coefficients to an approximately absolute scale, and to determine the value of the overall temperature exponent as $2B=6.8 \text{ \AA}^2$. Then, following Lipson & Cochran (1957), the coefficients were 'sharpened' by the function $(1/f)^2$, where f is the average scattering factor excluding thermal effects.

The sulphur and sodium coordinates were obtained without difficulty from the Patterson function; also, by searching for possible sulphur-light atom interactions, three tentative light-atom positions were found. The R index for structure factors based on the sulphur and sodium atoms was 61%. After inclusion, in turn, of the contributions from the three light atoms (considered as nitrogen), the R values were 58%, 61% and 62%. These results were taken as an indication that the sulphur, sodium, and first light atom had been correctly placed. (This subsequently proved to be the case; in addition, the second, but not the third, light-atom coordinates substantially agreed with those of a real atom.)

The first three-dimensional Fourier synthesis was calculated with the use of the signs given by the three known atoms. In this synthesis, the method of Woolfson (1956) was used to weight the magnitude of each coefficient according to the probability that its sign was correct. From the resultant synthesis, the remainder of the structure could be seen. R from the coordinates as known at this stage was 22% for the observed reflexions. The weighting system of Woolfson was most successful in this application, for, although

the lowest peak density was 2.6 e. \AA^{-3} , the background density did not exceed 1.3 e. \AA^{-3} .

Refinement of the structure

After two further Fourier syntheses had reduced R to 17%, subsequent refinement was by the method of 'differential difference' Fourier syntheses (Cochran, 1951; Cruickshank, 1952, 1956a).

The combination of methods used to measure intensities made it difficult to assess the reliability of an individual F_o . From a comparison of repeated measurements it appeared, to a rough approximation, that the F_o 's had a constant absolute uncertainty. Therefore the coefficients $\Delta F=(F_o-F_c)$ were, in general, given unit weight. For those F_o 's observed as zero, but having $|F_m| < |F_c| < 2|F_m|$ (F_m being the observable threshold of F_o), the contribution $\Delta F=(F_m-F_c)$ was included. Terms for which $|F_c| < |F_m|$, or $|F_c| > 2|F_m|$, were omitted from the calculation. In the early stages of refinement, individual isotropic temperature factors were used for each atom. The first two refinement cycles reduced R to 13%. An inspection of the larger F_o 's suggested appreciable secondary extinction effects; a correction of the form described by James (1958) was therefore applied (see below). At this stage the six hydrogen atoms, all of which were bonded directly to the PTD molecule, were placed geometrically by assuming a C-H bond length of 1.05 \AA (Allen & Sutton, 1950). These hydrogen atoms were then given the temperature factor of their bonding carbon atom, and held constant while the remaining heavy atoms were refined for a further three cycles (to $R=10.4\%$). During the final cycle of refinement with isotropic temperature factors, the mean coordinate shift was 0.0011 \AA , and the greatest shift 0.0040 \AA , which was a quarter of the corresponding coordinate standard deviation.

By now it was apparent that some of the atoms had considerably anisotropic thermal motions, for, in some cases, the curvatures

$$\frac{\partial^2(\rho_o - \rho_c)}{\partial x^2}, \frac{\partial^2(\rho_o - \rho_c)}{\partial y^2} \text{ and } \frac{\partial^2(\rho_o - \rho_c)}{\partial z^2}$$

differed appreciably from zero (although the average of the three curvatures was small). Evidence of this anisotropy could also be seen in a three-dimensional difference synthesis calculated at this stage. This synthesis also confirmed the positions of all the hydrogen atoms except those at the extremity (*i.e.* in the vicinity of C(7)) of the benzene ring, where the electron density was modified, presumably by vibrational effects. The first three cycles of refinement with anisotropic temperature factors (hydrogens included but not refined) reduced R to 7.7%. Since the hydrogen positions had been estimated from bonding considerations, an effort was made to refine

these coordinates. No attempt was made to improve the thermal parameters, and, to guard against divergence, all the calculated coordinate shifts were halved. During refinement of the hydrogen atoms (other atoms being held constant), only those F_o 's with $\sin \theta < 0.4$ were included; for these, R remained constant (6.0%), but the sum of squares of the coefficients (*i.e.* $\Sigma(F_o - F_c)^2$, the least-squares residual) fell from 872 to 826 during four cycles. All the coordinate changes converged, the mean shift falling from 0.055 to 0.011 Å, and the greatest from 0.17 to 0.036 Å.

James (1958) has suggested a secondary extinction correction of the form

$$(F_o^2)_{\text{corr.}} = F_o^2/1 - 2gF_o^2.$$

By plotting $(1 - F_o^2/F_c^2)$ against F_o^2 for the more intense reflexions, as shown in Fig. 1, $2g$ was determined as 3.1×10^{-5} , and was then used to correct all the F_o 's.

After three further cycles refining the heavy atom parameters, the shifts became negligible; the mean coordinate shift was 0.0003 Å, the greatest 0.0017 Å

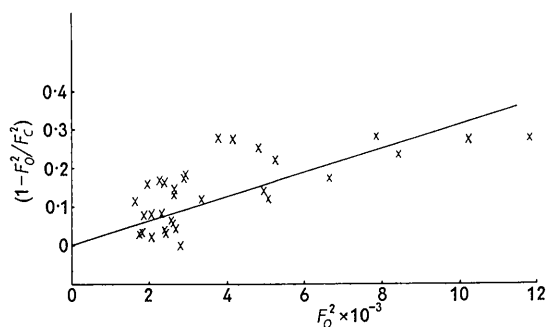


Fig. 1. Determination of the correction for secondary extinction.

Table 2. Final positional parameters and their standard deviations

Atom	x/a	y/b	z/c
S	0.4433 ± 0.0004	0.0927 ± 0.0004	0.1933 ± 0.0003
Na	0.1891 ± 0.0005	0.0102 ± 0.0006	0.0236 ± 0.0004
O(1)	0.2048 ± 0.0009	0.6917 ± 0.0010	0.0798 ± 0.0007
O(2)	0.9975 ± 0.0009	0.1003 ± 0.0010	0.0986 ± 0.0007
N	0.1226 ± 0.0010	0.3769 ± 0.0011	0.0803 ± 0.0008
C(1)	0.1314 ± 0.0011	0.5627 ± 0.0013	0.1093 ± 0.0009
C(2)	0.0285 ± 0.0011	0.2741 ± 0.0012	0.1165 ± 0.0009
C(3)	0.0510 ± 0.0013	0.6236 ± 0.0015	0.1838 ± 0.0010
C(4)	0.1529 ± 0.0014	0.6782 ± 0.0016	0.2725 ± 0.0011
C(5)	0.2472 ± 0.0018	0.5374 ± 0.0022	0.3197 ± 0.0013
C(6)	0.3452 ± 0.0023	0.5929 ± 0.0029	0.4003 ± 0.0015
C(7)	0.3520 ± 0.0027	0.7834 ± 0.0029	0.4302 ± 0.0018
C(8)	0.2667 ± 0.0038	0.9183 ± 0.0027	0.3844 ± 0.0020
C(9)	0.1626 ± 0.0023	0.8683 ± 0.0020	0.3040 ± 0.0014
H(1)	0.495 ± 0.015	0.779 ± 0.015	0.163 ± 0.012
H(2)	0.250 ± 0.017	0.374 ± 0.018	0.306 ± 0.013
H(3)	0.412 ± 0.018	0.458 ± 0.020	0.432 ± 0.014
H(4)	0.438 ± 0.019	0.805 ± 0.020	0.501 ± 0.015
H(5)	0.256 ± 0.022	0.034 ± 0.019	0.402 ± 0.015
H(6)	0.103 ± 0.018	0.949 ± 0.017	0.274 ± 0.014

(0.09σ); the greatest relative B_{ij} change was 2%, except for some of the small B_{12} and B_{23} , where the absolute changes were small. Finally, the hydrogen atom coordinates were refined for another four cycles, during the last of which the mean shift was 0.0059 Å, and the greatest 0.019 Å (0.14σ).

The final refined atomic parameters are listed in Tables 2 and 3. The coordinate standard deviations were found by using the formulae of Cruickshank (1949), *e.g.*

$$\sigma(x_n) = \frac{2\pi}{aV_c} \{ \Sigma h^2 (F_o - F_c)^2 \}^{1/2} \left(\frac{\partial^2 \rho_c}{\partial x^2} \right)_n.$$

Table 4 lists the observed and calculated structure factors; for those with measurable intensities, the final R index was 6.9%.

Table 3. Final anisotropic thermal parameters ($\times 10^4$)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	110	269	55	17	58	9
Na	95	243	53	-14	34	14
O(1)	110	245	53	-2	37	19
O(2)	123	228	58	1	17	8
N	107	173	48	21	23	15
C(1)	91	218	45	36	13	31
C(2)	100	187	48	-5	11	2
C(3)	108	284	47	51	23	13
C(4)	121	319	51	-15	37	-30
C(5)	184	506	71	106	-47	-57
C(6)	250	676	74	150	-85	-21
C(7)	266	593	82	-203	-31	-34
C(8)	395	392	80	-219	36	-58
C(9)	259	341	57	-70	28	-12

H(1) as C(3)
H(2) as C(5)
H(3) as C(6)
H(4) as C(7)
H(5) as C(8)
H(6) as C(9)

Computations

Most computations were made on an IBM 7090 computer; however at a late stage an IBM 1620 computer became available, and was also used. All the programs used were written by the author.

In the IBM 7090 'structure refinement' program, use was made of refinement expressions given by Cruickshank (1952, 1956a), and Dunitz & Rollett (1956). Individual scaling factors were necessary for each layer of constant k ; these were determined from the criteria that $\Sigma F_o = \Sigma F_c$, and were applied to the F_o 's before the other shifts were evaluated from the coefficients ($F_o - F_c$).

The atomic scattering factor curves of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used for Na, O, N and C; that of Dawson (1960) for S, and that of McWeeny (1951) for H. These were read into the computer at intervals of 0.005 in $\sin \theta/\lambda$ and were used without interpola-

Table 4. Observed and calculated structure factors

Within each group of constant h and k , the columns contain from left to right: I , $10F_o$ and $10F_c$. An asterisk indicates the estimated minimum observable F_o for reflexions which were too weak to be measured

0 0 L	-6 0 L	1 1 L	4 1 L	10 1 L	11 1 L	-2 2 L	-5 2 L	9 2 L
1 800 974	1 52* 53	0 364 418-	0 40* 23	0 122 115	1 134 154-	1 47* 32-	0 61* 18	
2 50 46-	2 183 198	1 84 93-	1 291 292-	1 129 135-	1 93 115-	2 240 226-	1 42 35-	
3 45 50-	3 373 379	2 553 588	2 120 102-	2 210 224-	2 49 53	3 133 126-	3 461 422-	
4 486 520-	4 169 181	3 646 725	3 197 208-	3 163 159-	3 37* 9-	4 51 54	4 79 76-	
5 69 55-	5 103 91-	4 216 229	4 191 94	4 119 113-	4 31* 21-	5 37* 13	5 120 90	
6 290 265-	6 176 158-	5 307 334-	5 373 384	5 63* 30		6 183 189-	6 137 108-	
7 107 93-	7 233 203	6 457 467-	6 303 305	6 64* 36-	-11 1 L	7 111 101-	7 143 156-	
8 311 299-	8 360 350	7 51 40-	7 76 61	7 173 177-		8 115 95-	8 251 260-	
9 64 59	9 271 279	8 50* 18	8 136 143-	8 96 98-		9 95 78-	9 117 103	
10 534 521	10 111 120	9 149 139-	9 62* 29-	9 57* 18-		10 207 219	10 255 246	
11 275 275	11 71 57-	10 197 203-	10 63* 33-	10 53* 7		11 170 171	11 127 119	
12 63* 7-	12 64* 35-	11 284 293-	11 62 51	11 46* 22		12 103 103	12 36 38-	
13 165 144-	13 77 75	12 82 66-	12 76 75-	12 38* 27-		13 51 62	13 78 80-	
14 113 121-	14 99 102	13 108 97	13 51 50-			14 125 124	14 41 39-	
15 60* 20	15 56* 12-	14 62* 34-	14 50* 7	-7 1 L		15 56 59	15 54* 16	
16 55* 42	16 91 91-	15 89 84-	15 24* 30			16 54* 12	16 48* 38	
17 52 44-	17 48* 22-	16 84 81-	16 62 45	1 109 115		17 44* 11-	17 39* 26-	
18 43 59-	18 57 50	17 41* 43-		2 59 62		18 33* 17-	18 24* 74-	
		18 25* 10		3 149 159-				6 61* 37-
				4 59* 14-				7 60* 3
				5 184 180				8 96 89
				6 75 69				9 100 94
				7 61* 32				10 55* 2
				8 145 136-				11 85 81-
				9 63* 38				12 81 72-
				10 157 157				13 20* 23-
				11 188 181				14 35* 27
				12 76 79				
				13 59* 2				
				14 55* 6-				
				15 64 56				
				16 76 89				
				17 32* 40				
				8 1 L				
				0 63* 2-				
				1 63* 7-				
				2 120 126-				
				3 88 73-				
				4 63* 27-				
				5 62* 4				
				6 75 69				
				7 56 51				
				8 56 49				
				9 48* 17-				
				10 51 44				
				11 58 44				
				12 88 80				
				13 79 72				
				14 66 58				
				15 58 51				
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				1 176 161				
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				4 239 237				
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				6 84 80				
				7 119 112				
				8 95 78				
				9 146 143				
				10 164 158				
				11 61* 15-				
				12 51 45-				
				13 50* 13				
				14 42 19				
				15 29* 20-				
				16 68 63				
				17 62 62				
				18 62* 19				
				19 61* 35				
				20 76 62				
				21 60* 9				
				22 50 52-				
				23 51 47-				
				24 33* 3				
				0 9 1 L				
				0 73 75				
				1 84 79				
				2 46 55-				
				3 67 62				
				4 54 58				
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				3 173 174-				
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				6 62* 3-				
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				9 61* 8				
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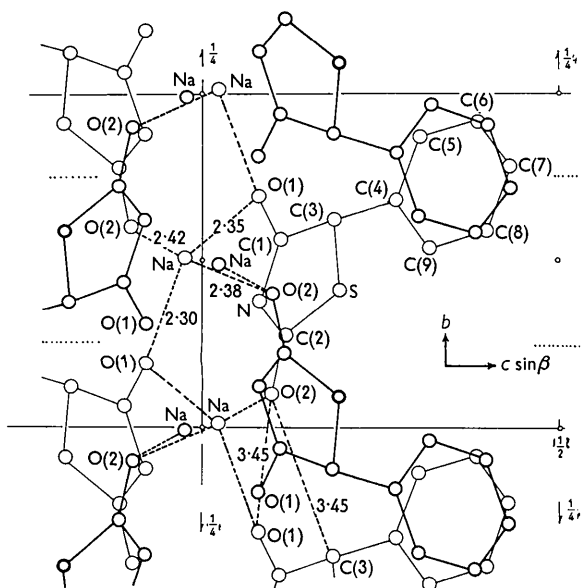


Fig. 2. Sodium atom bonding.

The phenylthiazolidine molecule

The bond lengths and angles of the PTD molecule are given in Table 5, and illustrated diagrammatically in Fig. 4. In some cases the coordinate s.d.'s $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ of an atom differed appreciably; this was taken into account in the bond length and angle calculations by using the formulae given by Ahmed & Cruickshank (1953). The bond lengths are within normal limits except for the short C(7)-C(8) bond (1.314 Å), for which the departure from the expected value of 1.395 Å is 'possibly significant' in terms of

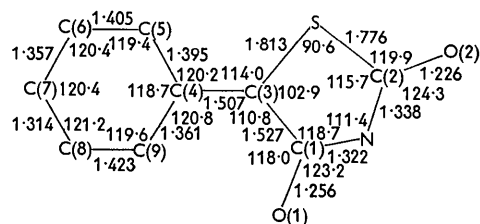


Fig. 4. Intramolecular bond lengths and angles.

Table 5. Final bond lengths and angles, and their standard deviations

Atoms	Length	Atoms	Angle
S-C(2)	1.776 ± 0.011 Å	S-C(3)-C(1)	102.9 ± 1.3°
S-C(3)	1.813 ± 0.011	C(3)-C(1)-N	118.7 ± 1.6
N-C(2)	1.322 ± 0.012	C(1)-N-C(2)	111.4 ± 1.5
N-C(1)	1.338 ± 0.014	N-C(2)-S	115.7 ± 1.3
C(1)-C(3)	1.527 ± 0.016	C(2)-S-C(3)	90.6 ± 0.9
C(1)-O(1)	1.256 ± 0.013	O(1)-C(1)-N	123.2 ± 1.6
C(2)-O(2)	1.226 ± 0.011	O(1)-C(1)-C(3)	118.0 ± 1.6
C(3)-C(4)	1.507 ± 0.018	O(2)-C(2)-N	124.3 ± 1.7
C(4)-C(5)	1.395 ± 0.020	O(2)-C(2)-S	119.9 ± 1.4
C(5)-C(6)	1.405 ± 0.025	C(4)-C(3)-C(1)	110.8 ± 1.6
C(6)-C(7)	1.357 ± 0.027	C(4)-C(3)-S	114.0 ± 1.4
C(7)-C(8)	1.314 ± 0.034	C(3)-C(4)-C(5)	120.2 ± 2.0
C(8)-C(9)	1.424 ± 0.034	C(3)-C(4)-C(9)	120.8 ± 2.1
C(9)-C(4)	1.361 ± 0.018	C(4)-C(5)-C(6)	119.4 ± 2.5
C(3)-H(1)	0.87 ± 0.12	C(5)-C(6)-C(7)	120.4 ± 3.1
C(5)-H(2)	1.12 ± 0.12	C(6)-C(7)-C(8)	120.4 ± 3.7
C(6)-H(3)	1.15 ± 0.15	C(7)-C(8)-C(9)	121.2 ± 3.9
C(7)-H(4)	1.20 ± 0.18	C(8)-C(9)-C(4)	119.6 ± 3.0
C(8)-H(5)	0.84 ± 0.13	C(9)-C(4)-C(5)	118.7 ± 2.3
C(9)-H(6)	0.85 ± 0.15		

the significance levels of Cruickshank & Robertson (1953). All the atoms of the benzene ring have con-

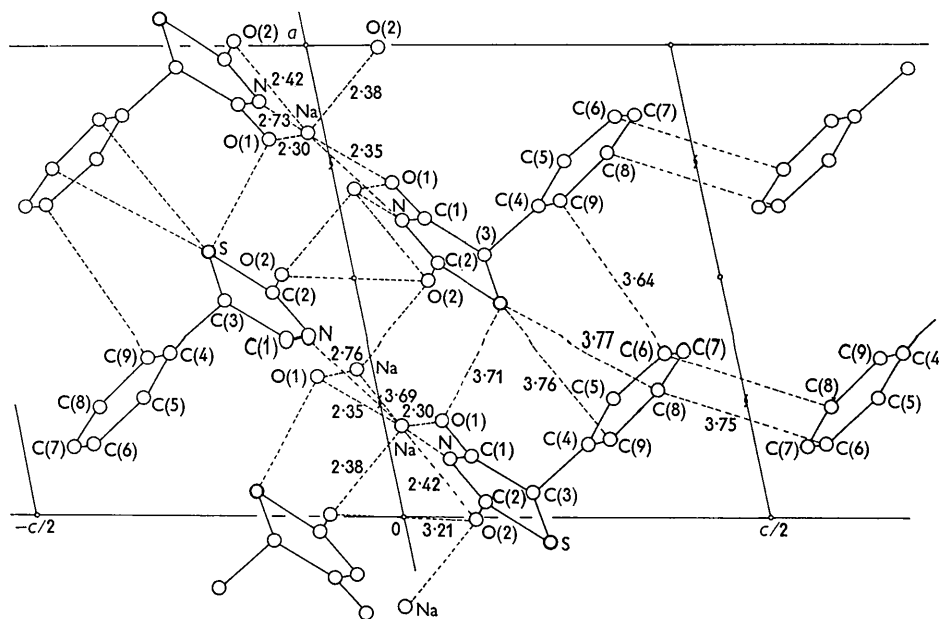


Fig. 3. Intermolecular distances less than 4.0 Å. Two close approaches that cannot be shown here are shown in Fig. 2.

siderable thermal motion ('isotropic' refinement gave values of '*B*' increasing across the benzene ring from 4.4 Å² for C(4), to 9.0 Å² for C(7)). It is thought that any apparent departures of the benzene ring from regularity are due to this extreme thermal motion (Cruickshank, 1956b).

The bond lengths of the thiazolidine ring can be satisfactorily accounted for by a combination of resonance structures. The formula of Pauling (1948) was used to calculate the double bond character of each bond, the single- and double-bond lengths being

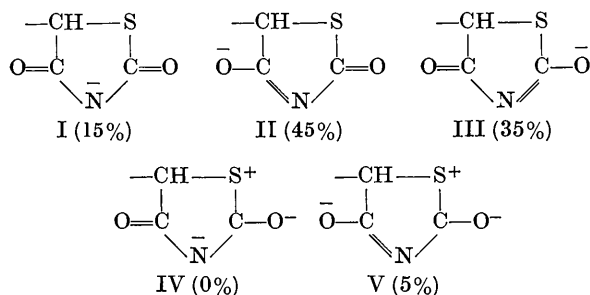


Fig. 5. Some canonical formulae for the thiazolidine ring.

assumed to be C-C, 1.54; C-N⁻, 1.50; C=N, 1.27; C-O⁻, 1.45; C=O, 1.20; C-S, 1.81; and C=S⁺, 1.61 Å (cf. Gerdil, 1961). On combining the canonical formulae in the proportions shown in Fig. 5, the calculated bond lengths were found to be in good agreement with those observed; the agreement is shown in Table 6.

Table 6. Comparison of bond lengths of the thiazolidine ring

The calculated bond lengths are found by using the valence bond method in combining the canonical formulae I-V in the proportions shown in Fig. 5

Bond	Observed length	Calculated length
S-C(3)	1.81 Å	1.81 Å
S-C(2)	1.78	1.78
C(3)-C(1)	1.53	1.54
C(1)-N	1.32	1.33
C(2)-N	1.34	1.36
C(1)-O(1)	1.26	1.26
C(2)-O(2)	1.23	1.24

The best-fitting plane through the six benzene-ring atoms, calculated by the least-squares method of Schomaker, Waser, Marsh & Bergman (1959), is

$$7.670x + 1.420y - 10.631z = 0.753$$

where the distance from this plane to the origin is 0.753 Å. None of the atoms depart significantly from planar, the individual deviations being as follows: C(4), -0.007; C(5), 0.014; C(6), -0.012; C(7), -0.007; C(8), 0.017; C(9), 0.002 Å.

The best plane through the five thiazolidine ring atoms (S, C(3), C(1), N, C(2)) is

$$-5.536x + 2.013y - 9.209z = 0.651.$$

The departures from planarity of the ring atoms, and the attached O(1) and O(2) atoms, are as follows: S, 0.0045; C(3), -0.069; C(1), 0.050; N, -0.009; C(2), -0.028; O(1), 0.176; O(2), -0.041 Å. In this case the departures of C(1) and C(3) are considerable. In order to test whether the ring is, in fact, significantly aplanar, the χ^2 test was applied (Wheatley, 1953). Summing over the five ring atoms, $\chi^2 = 61.2$. From the table of Fisher (1954), this corresponds to a probability *P* less than 0.01 that the observed value of χ^2 is due to chance. The ring is, therefore, significantly aplanar. The plane through the four atoms involved in resonance (*i.e.* S, C(1), N, C(2)) is

$$-5.597x + 1.757y - 9.319z = 0.768.$$

In this case the departures are much less, *viz.* S, -0.0002; C(1), 0.0003; N, -0.004; C(2), 0.005 Å. Summing over these four atoms, $\chi^2 = 0.44$, and the corresponding value of *P* (=0.50) does not imply any significant departure from planarity. The other three atoms of interest have the following deviations from the plane: C(3), -0.134; O(1), 0.095; O(2), 0.040 Å. The best plane through the six atoms S, C(1), N, C(2), O(1) and O(2) (*i.e.* excluding C(3)) was also found. In this case $\chi^2 = 61.3$, indicating highly significant aplanarity.

Thermal vibrations

In order to examine the anisotropy of the atomic vibrations more conveniently, the vibrations were expressed in terms of the principal axes of the ellipsoids of vibration by using the transformation of Rollett & Davies (1955). Table 7 lists the parameters of the vibration ellipsoids which are defined by expressing the temperature factors in the form

$$T = \exp \left[-\frac{1}{4} \sum_i B_i (hg_{i1}a^* + kg_{i2}b^* + lg_{i3}c^*)^2 \right].$$

The B_i are the lengths of the principal axes, and the g_{i1} , g_{i2} and g_{i3} are the direction cosines of these axes with respect to a^* , b^* and c^* . As might be expected, the more tightly bound thiazolidine ring atoms have smaller thermal motions than those in the benzene ring, which is only bonded at C(4). At the extremity of the benzene ring the anisotropy is considerable, with, in general, the directions of minimum motion not far from parallel to the C(3)-C(4) bond, as might be anticipated.

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Table 7. *Principal axis thermal parameters*

Atom	<i>i</i>	<i>B_i</i> (Å ²)	<i>g_{i1}</i>	<i>g_{i2}</i>	<i>g_{i3}</i>
S	1	1.37	0.790	-0.055	-0.432
	2	2.15	0.447	-0.733	0.595
	3	1.96	0.420	-0.678	0.678
Na	1	1.38	0.944	0.213	-0.049
	2	1.99	0.018	0.731	0.670
	3	1.76	0.330	-0.648	0.741
O(1)	1	1.60	0.846	0.279	-0.266
	2	2.02	0.130	0.718	0.696
	3	1.74	0.517	-0.638	0.667
O(2)	1	1.70	0.664	-0.626	0.539
	2	1.77	0.602	0.772	0.325
	3	2.22	-0.443	0.111	0.777
N	1	1.62	0.887	0.407	0.398
	2	1.26	-0.349	0.900	-0.328
	3	1.75	-0.301	0.155	0.857
C(1)	1	1.16	0.769	-0.469	0.587
	2	1.88	0.102	0.761	0.648
	3	1.64	-0.632	-0.448	0.486
C(2)	1	1.39	0.853	0.293	0.601
	2	1.44	-0.227	0.954	-0.241
	3	1.86	-0.470	0.071	0.762
C(3)	1	1.46	0.853	-0.352	0.555
	2	2.29	0.366	0.930	0.114
	3	1.70	-0.371	0.109	0.824
C(4)	1	1.79	0.981	0.160	0.310
	2	2.53	-0.122	0.948	-0.313
	3	1.67	-0.148	0.276	0.898
C(5)	1	1.70	0.740	-0.007	0.813
	2	4.76	0.493	0.685	-0.420
	3	3.10	-0.457	0.728	0.404
C(6)	1	4.44	0.459	-0.729	-0.400
	2	6.10	0.574	0.680	-0.326
	3	1.69	0.678	-0.082	0.857
C(7)	1	2.17	0.655	0.315	0.687
	2	5.63	0.673	-0.565	-0.341
	3	4.06	-0.343	-0.686	0.642
C(8)	1	6.44	0.930	-0.302	-0.009
	2	2.22	0.366	0.718	0.656
	3	3.24	-0.029	-0.627	0.755
C(9)	1	4.08	0.941	-0.239	-0.037
	2	2.55	0.177	0.951	-0.212
	3	1.96	0.289	0.198	0.976

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