

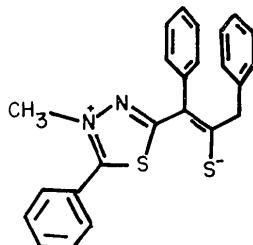
# The Crystal Structure of C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>S<sub>2</sub>. A New Mesoionic Thiadiazole Derivative

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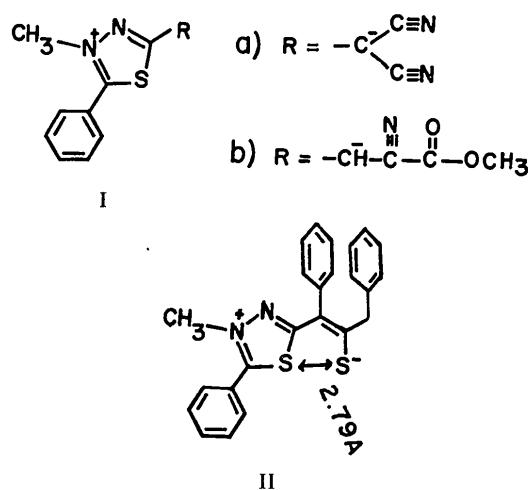
The stereochemistry of a new mesoionic thiadiazole derivative



(C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>S<sub>2</sub>) has been established by X-ray analysis. The two sulfur atoms, which are in a *syn* conformation with respect to one another, are separated by only 2.79 Å. The material crystallizes in the monoclinic space group P<sub>2</sub><sub>1</sub>/n with *a* = 14.673 (2), *b* = 11.037 (2), *c* = 12.995 (2) Å, β = 102.1 (1)° and *Z* = 4. The 3325 X-ray data were collected on an automatic diffractometer and refined by least-squares procedures to a final *R* value of 0.061. The structure was solved using the symbolic addition procedure.

## Introduction

The first syntheses of mesoionic 1,3,4-thiadiazoles (I) in which a carbon atom occupies the exocyclic position at C(2) have recently been reported (Grashey, Baumann & Hamprecht, 1970). The synthesis of the molecule to be discussed here (II) was then carried out by Moriarty and Mukherjee since a compound having a CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> group exocyclic on C(2) would be of significant theoretical and synthetic interest. Spectral evidence indicated the structural formula of the molecule and the X-ray analysis confirmed the molecular formula and established the stereochemistry of the molecule (Moriarty, Mukherjee, Flippin & Karle, 1971). The intramolecular relationship between the two sulfur atoms was of particular interest and the X-ray study showed them to be in a *syn* conformation.



## Experimental

One red, gem-like crystal of this material was provided by Professor R. M. Moriarty of the University of Illinois. However, the size of the crystal (~4 × 2.5 × 1.5 mm) precluded its use for data collection. The 3325 X-ray data [maximum (sin θ)/λ = 0.557] were obtained at room temperature on a four-circle computer controlled diffractometer using the θ-2θ technique with a 1.8 + 2θ(α<sub>2</sub>) - 2θ(α<sub>1</sub>) scan over 2θ from one of the small irregularly shaped fragments which resulted from attempts to cut the original crystal. The scanning speed was 2° per min and backgrounds were counted for 10 sec. All reflections collected were included in the data set; no intensities were considered to be 'unobserved'.

The molecule, C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>S<sub>2</sub>, crystallizes in the monoclinic space group P<sub>2</sub><sub>1</sub>/n with *a* = 14.673 (2), *b* = 11.037 (2), *c* = 12.995 (2) Å and β = 102.1 (1)°. The cell parameters and their standard deviations are based on a least-squares refinement of the diffractometer coordinates of twelve independent reflections. There are four molecules per unit cell corresponding to a crystallographic density of 1.29 g.cm<sup>-3</sup>. The absorption coefficient for this molecule is 29.46 cm<sup>-1</sup>. The maximum μ<sub>R</sub> is 1.5.

The structure was solved using the symbolic addition procedure for centrosymmetric crystals (Karle & Karle, 1963, 1966). The implementation of the Σ<sub>2</sub> formula was facilitated by using a computer program written by R. D. Gilardi of this laboratory. The structure was refined using the full-matrix least-squares methods (Busing, Martin & Levy, 1962) with the weighting function 1/w = (|F<sub>o</sub>|/15)<sup>2</sup> + 1.0 which was suggested by a statistical examination of the least-squares discrepancies. The function minimized was  $\sum w(F_o - F_c)^2$ .

Table 1. Fractional coordinates and thermal parameters with standard deviations

Thermal parameters are of the form

$$T = \exp[-\frac{1}{2}(B_{11}h^2a^* + B_{22}k^2b^* + B_{33}l^2c^* + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)].$$

The  $B_{ij}$ 's are in  $\text{\AA}^2$ .

Standard deviations are based solely on least-squares parameters.

	<i>X</i>	<i>Y</i>	<i>Z</i>	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
S(1)	0.37515(4)	0.54220(6)	-0.01420(4)	2.18(3)	2.49(3)	1.85(3)	-0.13(2)	0.07(2)	-0.09(2)
C(2)	0.43459(15)	0.56443(23)	0.11669(18)	2.13(9)	2.74(10)	2.29(9)	0.23(7)	0.35(7)	-0.04(8)
N(3)	0.43609(15)	0.46851(18)	0.17730(17)	3.10(9)	2.39(8)	2.60(9)	0.03(7)	0.05(7)	-0.24(7)
N(4)	0.38577(15)	0.37741(19)	0.12204(17)	3.14(9)	2.17(8)	2.78(9)	-0.05(7)	0.28(7)	-0.09(7)
C(5)	0.34829(16)	0.39796(22)	0.02172(20)	2.90(9)	2.81(10)	2.98(10)	0.01(7)	0.72(8)	-0.21(8)
C(6)	0.47535(16)	0.67640(23)	0.15883(19)	2.47(9)	2.71(10)	2.62(10)	-0.02(8)	0.42(8)	-0.20(8)
C(7)	0.47199(17)	0.77893(23)	0.09864(20)	2.99(10)	2.96(11)	2.99(11)	-0.28(8)	0.54(8)	0.01(8)
S(8)	0.42844(5)	0.78236(6)	-0.03356(5)	3.05(3)	3.13(3)	2.39(3)	-0.42(2)	0.12(2)	0.59(2)
C(9)	0.50227(19)	0.89896(23)	0.15356(22)	3.09(11)	2.67(10)	3.60(12)	-0.47(8)	0.62(9)	0.03(9)
C(10)	0.43191(19)	0.94400(22)	0.21470(22)	3.18(11)	2.03(9)	3.68(12)	-0.19(8)	0.58(9)	0.16(8)
C(11)	0.46089(23)	0.98435(28)	0.31739(25)	4.16(14)	3.56(12)	3.87(13)	-0.07(10)	0.45(11)	0.14(10)
C(12)	0.39759(24)	1.02979(33)	0.37503(27)	6.15(16)	4.20(17)	4.54(16)	0.02(14)	2.16(13)	0.13(14)
C(13)	0.30394(29)	1.03423(33)	0.32706(36)	6.49(19)	4.07(16)	7.49(23)	-0.10(13)	3.94(17)	0.20(15)
C(14)	0.27364(23)	0.99400(30)	0.22499(36)	3.77(14)	3.74(13)	3.40(24)	0.16(10)	2.03(15)	-0.13(14)
C(15)	0.33724(21)	0.94891(27)	0.16919(28)	3.64(12)	3.32(12)	5.49(16)	-0.15(9)	0.43(11)	-0.56(11)
C(16)	0.51724(19)	0.67689(22)	0.27458(20)	3.73(11)	2.17(9)	2.55(10)	-0.08(8)	0.26(9)	-0.21(8)
C(17)	0.61354(20)	0.68672(29)	0.31018(26)	3.72(12)	4.33(13)	4.16(14)	0.42(10)	-0.68(10)	-0.55(11)
C(18)	0.65307(28)	0.69033(37)	0.41610(30)	6.37(17)	5.77(17)	4.20(17)	1.33(14)	-1.34(14)	-0.77(13)
C(19)	0.59806(34)	0.68141(38)	0.48801(30)	9.03(24)	5.74(18)	3.55(15)	0.77(17)	-1.27(15)	-0.44(13)
C(20)	0.50144(35)	0.67135(37)	0.45574(10)	10.42(26)	5.20(17)	3.55(15)	-1.10(17)	2.61(16)	-0.54(13)
C(21)	0.46190(24)	0.66914(28)	0.34814(24)	5.91(16)	4.11(13)	3.35(13)	-1.10(12)	1.29(11)	-0.33(10)
C(22)	0.28762(19)	0.31445(25)	-0.04996(21)	2.80(11)	3.46(11)	3.14(11)	-0.51(9)	0.44(9)	-0.68(9)
C(23)	0.30643(22)	0.19088(28)	-0.05388(25)	3.98(13)	3.55(12)	4.01(14)	0.84(10)	0.76(11)	-0.87(10)
C(24)	0.24705(25)	0.11669(32)	-0.12370(28)	5.13(15)	4.50(15)	4.90(15)	-1.52(12)	0.93(13)	-1.39(12)
C(25)	0.17011(25)	0.16447(34)	-0.18943(30)	4.85(16)	6.07(16)	4.90(16)	-1.44(13)	0.09(13)	-2.09(13)
C(26)	0.15305(24)	0.28812(40)	-0.18944(32)	3.91(13)	7.13(22)	5.14(18)	-0.03(13)	-1.06(12)	-1.56(15)
C(27)	0.21144(20)	0.36401(32)	-0.11930(25)	3.47(11)	5.08(15)	4.14(13)	0.22(11)	-0.39(10)	-1.10(12)
C(28)	0.37529(25)	0.26910(27)	0.18296(25)	6.68(16)	2.80(11)	3.80(14)	-0.77(11)	0.46(12)	0.43(10)

Table 1 (cont.)

H(9A)	0.5621	0.8837	0.2023
H(9B)	0.5096	0.9558	0.0970
H(11)	0.5182	0.9615	0.3545
H(12)	0.4219	1.0566	0.4538
H(13)	0.2564	1.0601	0.3809
H(14)	0.2050	1.0044	0.1849
H(15)	0.3209	0.9133	0.0922
H(17)	0.6524	0.6909	0.2464
H(18)	0.7317	0.7113	0.4379
H(19)	0.6374	0.6811	0.5663
H(20)	0.4710	0.6662	0.5267
H(21)	0.4017	0.6734	0.3216
H(23)	0.3608	0.1526	-0.0076
H(24)	0.2748	0.0242	-0.1221
H(25)	0.1215	0.1122	-0.2578
H(26)	0.1028	0.3263	-0.2369
H(27)	0.1931	0.4564	-0.1165
H(28A)	0.3926	0.2903	0.2634
H(28B)	0.4186	0.2317	0.1766
H(28C)	0.3163	0.2351	0.1628

All the hydrogen atoms were located in a difference map but their positions were not refined. No absorption or extinction corrections were attempted owing to the extreme irregularity of the crystal fragment used to collect the data. However, those reflections showing severe secondary extinction effects (0.7% of the data) were omitted from the final cycle of refinement which reduced the  $R$  index to 0.061. The final  $R$  index for the full set (3325 reflections) of data was 0.078. Table 1 lists the coordinates and thermal parameters of each atom while the observed and calculated structure factors are compared in Table 2.

### Discussion

The stereoconfiguration of the molecule is illustrated in Fig. 1 and it shows that the two sulfur atoms are

in a *syn* conformation with respect to one another. The entire central portion of the molecule [atoms 1–9 and C(28)] is essentially planar ( $\pm 0.2$  Å) with ring *A* planar to within  $\pm 0.02$  Å. All three benzene rings are planar; ring *B* to within  $\pm 0.004$  Å, ring *C* to within  $\pm 0.007$  Å and ring *D* to within  $\pm 0.02$  Å. The torsion angles relating the benzene rings to the central plane are 48.9° for ring *B* [C(7)–C(9)–C(10)–C(15)], 71.8° for ring *C* [C(7)–C(6)–C(16)–C(17)], and 40.8° for ring *D* [S(1)–C(5)–C(22)–C(27)]. The bond distances and angles are shown in Fig. 2. The distribution of distances in ring *A* plus atoms C(6), C(7) and C(8) shows the foreshortening of single bonds and small increases in lengths of double bonds associated with conjugated systems. The S···S intramolecular distance is 2.79 Å which is too long to be considered analogous to the S–S ‘bond’ lengths of 2.23–2.57 Å exhibited in the thiathiaphthene systems (Hordvik, 1968; Johnson & Paul, 1969; Johnson, Newton & Paul, 1969). However, it is considerably shorter than the sum of the van der Waals radii of 3.70° for two sulfur atoms (Pauling, 1960), indicating a definite attraction between the two atoms. It is also shorter than the S···S distances of 2.91 Å reported for III (Beer, Frew, Johnson & Paul, 1970), ~2.95 Å for the two independent molecules of IV (Flippen & Karle, 1970) and 2.97 Å for V (Sletten, 1969) in which the sulfur atoms are in an environment similar to that found in the thiadiazole under discussion (II). A distance of 1.63 to 1.67 Å has been observed for the C=S bond in thiourea derivatives and other compounds studied in this laboratory (*e.g.* Karle, Estlin & Britts, 1967; Flippen & Karle, 1970). In these molecules there is no attraction between the sulfur

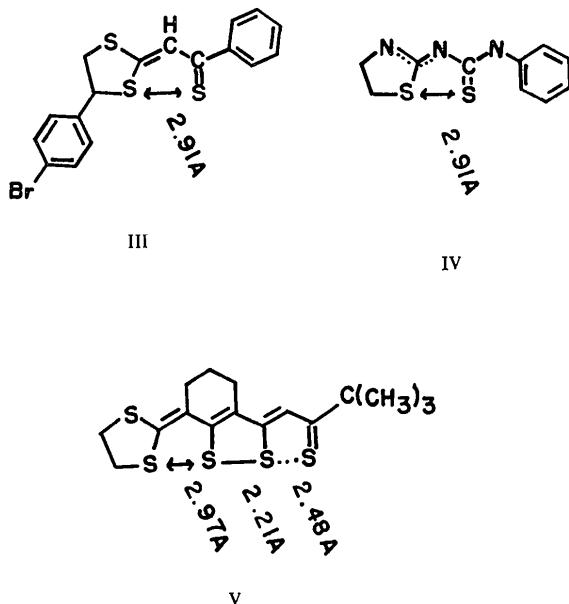
Table 2. Observed and calculated structure factors  
Column headings are index  $h$ ,  $|F_o| \times 10$ , and  $F_c \times 10$ .

$h$	$0 \pm 15$	$10 \pm 98$	$87 \pm 15$	$35 \pm 9$	$1 \pm 802 \pm 1295$	$1 \pm 115 \pm 126$	$15 \pm 51 \pm 56$	$6 \pm 130 \pm 139$	$11 \pm 31 \pm 30$	$6 \pm 336 \pm 330$	$0 \pm 17 \pm 27$	$2 \pm 923 \pm 161$	$\pm 4$	$7$	$3 \pm 270 \pm 286$	$1 \pm 20$
$5 \pm 33 \pm 37$	$14 \pm 147 \pm 198$	$13 \pm 158 \pm 193$	$3 \pm 59 \pm 72$	$1 \pm 15 \pm 15$	$1 \pm 14 \pm 15$	$1 \pm 149 \pm 231$	$7 \pm 254 \pm 256$	$12 \pm 65 \pm 56$	$7 \pm 187 \pm 185$	$1 \pm 189 \pm 185$	$3 \pm 550 \pm 549$	$0 \pm 81 \pm 82$	$2 \pm 70 \pm 285$	$1 \pm 34$	$2 \pm 342 \pm 331$	$1 \pm 20$
$5 \pm 40 \pm 45$	$14 \pm 147 \pm 198$	$13 \pm 158 \pm 193$	$3 \pm 59 \pm 72$	$1 \pm 15 \pm 15$	$1 \pm 149 \pm 231$	$7 \pm 254 \pm 256$	$12 \pm 65 \pm 56$	$7 \pm 187 \pm 185$	$1 \pm 189 \pm 185$	$3 \pm 550 \pm 549$	$0 \pm 81 \pm 82$	$2 \pm 70 \pm 285$	$1 \pm 34$	$2 \pm 342 \pm 331$	$1 \pm 20$	
$2 \pm 82 \pm 74$	$1 \pm 116 \pm 645$	$15 \pm 13 \pm 22$	$5 \pm 251 \pm 240$	$2 \pm 172 \pm 168$	$4 \pm 455 \pm 455$	$8 \pm 82 \pm 97$	$1 \pm 33 \pm 32$	$5 \pm 137 \pm 136$	$10 \pm 174 \pm 162$	$4 \pm 42 \pm 35$	$6 \pm 2 \pm 217$	$3 \pm 142 \pm 144$	$7 \pm 17 \pm 3$	$5 \pm 173 \pm 168$	$1 \pm 20$	
$4 \pm 58 \pm 75$	$1 \pm 129 \pm 151$	$1 \pm 17 \pm 20$	$6 \pm 404 \pm 395$	$3 \pm 121 \pm 125$	$1 \pm 111 \pm 115$	$3 \pm 39 \pm 39$	$10 \pm 216 \pm 204$	$12 \pm 286 \pm 287$	$11 \pm 203 \pm 194$	$7 \pm 17 \pm 17$	$5 \pm 2 \pm 17$	$3 \pm 142 \pm 144$	$7 \pm 17 \pm 3$	$5 \pm 173 \pm 168$	$1 \pm 20$	
$8 \pm 117 \pm 104$	$7 \pm 264 \pm 221$	$2 \pm 273 \pm 212$	$8 \pm 54 \pm 54$	$5 \pm 24 \pm 28$	$7 \pm 1 \pm 21$	$11 \pm 148 \pm 146$	$3 \pm 112 \pm 112$	$13 \pm 317 \pm 313$	$1 \pm 209 \pm 211$	$9 \pm 95 \pm 98$	$0 \pm 349 \pm 344$	$1 \pm 148 \pm 152$	$8 \pm 125 \pm 126$	$1 \pm 20$		
$1 \pm 73 \pm 74$	$9 \pm 127 \pm 114$	$3 \pm 31 \pm 27$	$9 \pm 204 \pm 204$	$6 \pm 132 \pm 128$	$6 \pm 598 \pm 584$	$12 \pm 254 \pm 252$	$10 \pm 204 \pm 201$	$14 \pm 25 \pm 22$	$1 \pm 209 \pm 211$	$10 \pm 142 \pm 141$	$8 \pm 2 \pm 19$	$1 \pm 148 \pm 152$	$8 \pm 125 \pm 126$	$1 \pm 20$		
$3 \pm 198 \pm 194$	$1 \pm 178 \pm 194$	$5 \pm 166 \pm 203$	$11 \pm 33 \pm 32$	$8 \pm 54 \pm 54$	$8 \pm 4 \pm 55$	$2 \pm 7 \pm 6$	$6 \pm 21 \pm 21$	$3 \pm 2 \pm 2$	$2 \pm 15 \pm 17$	$12 \pm 56 \pm 56$	$8 \pm 4 \pm 32$	$1 \pm 147 \pm 138$	$11 \pm 222 \pm 211$	$1 \pm 20$		
$9 \pm 28 \pm 21$	$1 \pm 0 \pm 6$	$6 \pm 217 \pm 209$	$12 \pm 50 \pm 47$	$4 \pm 222 \pm 222$	$1 \pm 147 \pm 147$	$9 \pm 966 \pm 927$	$0 \pm 32 \pm 5$	$7 \pm 49 \pm 49$	$0 \pm 747 \pm 638$	$1 \pm 147 \pm 147$	$10 \pm 23 \pm 26$	$1 \pm 42 \pm 81$	$1 \pm 209 \pm 202$	$1 \pm 20$		
$7 \pm 20 \pm 21$	$1 \pm 0 \pm 6$	$6 \pm 217 \pm 209$	$12 \pm 50 \pm 47$	$4 \pm 222 \pm 222$	$1 \pm 147 \pm 147$	$9 \pm 966 \pm 927$	$0 \pm 32 \pm 5$	$7 \pm 49 \pm 49$	$0 \pm 747 \pm 638$	$1 \pm 147 \pm 147$	$10 \pm 23 \pm 26$	$1 \pm 42 \pm 81$	$1 \pm 209 \pm 202$	$1 \pm 20$		
$9 \pm 190 \pm 184$	$2 \pm 45 \pm 74$	$6 \pm 134 \pm 127$	$1 \pm 24 \pm 24$	$12 \pm 14 \pm 13$	$1 \pm 15 \pm 20$	$2 \pm 147 \pm 151$	$1 \pm 130 \pm 112$	$2 \pm 73 \pm 65$	$5 \pm 67 \pm 59$	$5 \pm 10 \pm 103$	$1 \pm 147 \pm 147$	$5 \pm 5 \pm 5$	$1 \pm 147 \pm 147$	$5 \pm 5 \pm 5$		
$11 \pm 31 \pm 14$	$6 \pm 67 \pm 729$	$9 \pm 251 \pm 252$	$1 \pm 24 \pm 13$	$1 \pm 24 \pm 13$	$1 \pm 15 \pm 20$	$2 \pm 147 \pm 151$	$1 \pm 130 \pm 112$	$2 \pm 73 \pm 65$	$5 \pm 67 \pm 59$	$5 \pm 10 \pm 103$	$1 \pm 147 \pm 147$	$5 \pm 5 \pm 5$	$1 \pm 147 \pm 147$	$5 \pm 5 \pm 5$		
$1 \pm 6 \pm 12$	$8 \pm 25 \pm 222$	$10 \pm 176 \pm 176$	$1 \pm 24 \pm 24$	$1 \pm 24 \pm 24$	$1 \pm 15 \pm 20$	$3 \pm 31 \pm 20$	$12 \pm 130 \pm 124$	$10 \pm 158 \pm 156$	$3 \pm 2 \pm 23$	$6 \pm 2 \pm 21$	$3 \pm 142 \pm 144$	$2 \pm 205 \pm 205$	$1 \pm 147 \pm 147$	$2 \pm 217 \pm 192$		
$2 \pm 12 \pm 20$	$8 \pm 25 \pm 222$	$10 \pm 176 \pm 176$	$1 \pm 24 \pm 24$	$1 \pm 24 \pm 24$	$1 \pm 15 \pm 20$	$3 \pm 31 \pm 20$	$12 \pm 130 \pm 124$	$10 \pm 158 \pm 156$	$3 \pm 2 \pm 23$	$6 \pm 2 \pm 21$	$3 \pm 142 \pm 144$	$2 \pm 205 \pm 205$	$1 \pm 147 \pm 147$	$2 \pm 217 \pm 192$		
$6 \pm 47 \pm 76$	$10 \pm 115 \pm 124$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$		
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 145 \pm 155$	$2 \pm 245 \pm 256$	$1 \pm 20$			
$6 \pm 47 \pm 76$	$12 \pm 114 \pm 122$	$6 \pm 191 \pm 181$	$10 \pm 155 \pm 155$	$6 \pm 292 \pm 254$	$12 \pm 142 \pm 142$	$6 \pm 51 \pm 47$	$2 \pm 70 \pm 70$	$2 \pm 650 \pm 650$	$1$							

Table 2 (cont.)

2	30	2*	12	16	-19	3	25	-37	6	105	1n2	1d	26	+16	9	33	-28	6	129	13n	2	45b	47b	7	217	201	3	153	163	3	237	229	5	57	58	4	12	-1	0	81	-73		
3	665	-111	13	51	-49	4	239	-223	5	248	241	1d	123	+12	10	38	-41	7	117	-123	2	45b	47b	8	217	201	6	65	61	5	20	-15	1	40	-10								
4	302	-210	14	52	-47	5	27	15	6	190	144	1d	29	+31	11	293	287	8	73	76	4	391	384	9	104	-100	5	166	172	4	67	-11	6	62	55	2	173	-189					
5	85	84	15	74	75	6	186	-181	7	104	145	1d	188	-180	12	93	86	9	104	100	6	170	178	6	142	134	8	323	-321	7	135	133	3	76	76								
6	352	-49	16	49	48	4	403	391	5	100	-90	2	98	103	0	85	85	8	8	+8	6	274	-254	1	70	304	7	53	52	5	20	-15	5	30	-23								
7	352	-49	16	49	48	4	403	391	5	100	-90	2	98	103	0	85	85	8	8	+8	6	274	-254	1	70	304	7	53	52	5	20	-15	5	30	-23								
8	90	86	2	187	164	9	98	93	10	69	-47	3	167	157	1	108	103	1	169	174	8	220	-227	2	313	313	9	105	-103	4	175	-175	10	36	-17	0	144	-19					
9	319	36	3	10	92	159	1	159	159	1	234	-157	2	59	-52	1	157	127	3	81	79	10	44	-46	10	241	-250	1	48	-50	2	131	-127	0	80	63							
10	113	122	4	141	124	5	186	-181	7	104	145	1d	188	-180	12	93	86	9	104	100	10	170	178	10	147	134	11	150	150	11	50	50	10	30	-10								
11	143	-11	5	185	176	12	33	24	2	44	-47	4	663	363	4	71	64	4	47	37	10	202	194	9	104	100	5	125	-99	3	160	159	5	10	-5	5	20	-5					
12	149	11	6	170	6	6	7	117	117	6	76	63	2	348	-342	6	348	-342	7	121	-116	7	213	200	2	155	154	5	238	-230	5	10	-5	5	10	-5							
13	39	-30	7	117	117	6	76	63	2	348	-342	6	348	-342	7	121	-116	7	213	200	2	155	154	5	238	-230	5	10	-5	5	10	-5											
14	36	-29	8	98	-19	2	304	291	9	116	-181	10	101	-300	8	158	139	8	70	70	9	148	-510	4	389	-407	4	243	-259	7	166	164	0	52	-51	4	40	-37					
15	121	-129	10	503	483	3	262	219	7	281	-250	11	61	-63	9	173	174	9	149	-152	1	367	-400	0	78	72	5	57	-60	5	120	-108	1	17	-16	5	31	31					
16	276	249	10	503	483	3	262	219	7	281	-250	11	61	-63	9	173	174	9	149	-152	1	367	-400	0	78	72	5	57	-60	5	120	-108	1	17	-16	5	31	31					
17	345	36	12	149	149	1	237	216	1	149	-149	11	91	-76	11	90	-72	2	210	-227	6	264	-260	1	242	-254	10	223	230	1	132	-115	5	10	-5	5	20	-5					
18	519	377	13	70	77	6	112	-103	11	112	112	1	147	139	6	7	6	7	6	183	164	6	62	-50	8	156	-162	8	79	77	10	40	-2	4	42	-40	11	4					
19	216	-210	14	144	-198	7	102	-101	11	90	-64	4	216	-201	6	220	-220	5	217	-209	9	90	84	9	112	114	1	68	64	5	35	29	0	14	-10								
20	7	9	14	14	14	1	149	149	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149					
21	8	277	-271	0	54	54	4	146	-100	1	74	-73	2	233	-232	2	548	-557	1	111	100	9	152	-152	0	81	-83	3	59	-58	5	40	-40	1	131	-130							
22	9	70	70	14	50	12	16	-118	11	118	118	1	361	-316	1	145	-147	3	161	-164	8	98	93	12	182	-187	1	62	-85	5	120	126	3	74	76								
23	104	23	2	30	-30	11	118	-118	11	118	-118	1	361	-316	1	145	-147	3	161	-164	8	98	93	12	182	-187	1	62	-85	5	120	126	3	74	76								
24	294	201	14	144	-147	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149								
25	149	-149	8	317	217	0	14	-14	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149	1	149	-149								
26	121	-21	0	187	-198	0	146	-150	5	71	-63	5	63	-59	0	100	100	5	71	-63	5	63	-59	0	144	-144	5	247	-227	9	174	-182	8	94	-94	8	107	-103	4	48	-52	11	7
27	10	19	1	177	173	4	144	-144	0	111	-114	5	93	-76	7	84	-76	10	42	-76	2	328	-349	0	105	-113	9	93	-99	5	189	-220	0	160	101								
28	130	-34	5	171	170	3	122	-121	8	35	-35	7	151	-135	9	117	104	9	72	-75	11	215	-271	3	216	-217	10	152	150	4	226	-226	5	10	-5	5	20	-5					
29	554	-553	5	171	170	3	122	-121	8	35	-35	7	151	-135	9	117	104	9	72	-75	11	215	-271	3	216	-217	10	152	150	4	226	-226	5	10	-5	5	20	-5					
30	122	-102	4	284	-257	4	172	-165	7	19	-17	0	261	-265	8	107	104	10	151	-151	2	216	-218	3	242	-211	10	130	-125	3	37	-48	1	125	-265								
31	134	-142	5	409	-304	5	236	-226	10	49	-49	4	222	-229	0	107	-104	10	150	-150	6	400	-410	4	216	-215	10	130	-125	3	37	-48	1	125	-130								
32	133	-114	5	174	-164	5	174	-164	11	174	-174	1	346	-336	7	207	-205	3	194	-194	10	151	-151	3	242	-218	10	130	-125	3	37	-48	1	125	-130								
33	121	-114	7	47	-62	7	41	-41	12	117	-173	2	337	-337	8	205	-205	10	151	-151	3	242	-218	10	130	-125	3	37	-48	1	125	-130											
34	122	-202	2	241	-229	8	178	-199	1	192	-147	7	41	-41	3	197	-197	10	151	-151	3	242	-218	10	130	-125	3	37	-48	1	125	-130											
35	122	-202	2	241	-229	8	178	-199	1	192	-147	7	41	-41	3	197	-197	10	151	-151	3	242	-218	10	130	-125	3	37	-48	1	125	-130											
36	122	-202	2	241	-229	8	178	-199	1	192	-147	7	41	-41	3	197	-197	10	151	-151	3	242	-218	10	130	-125	3	37	-48	1	125	-130											
37	127	-254	6	53	-43	3	35	-20	13	145	-193	7	21	-21	2	229	-280	10	217	-219	11	178	-118	10	104	-101	1	148	-200	5	159	-174											
38	20	-44	7	110	-110	1	147	-147	12	146	-146	3	58	-58	1	145	-145	6	51	-48	1	145	-145	6	51	-48	1	145	-145	6	51	-48	1	145	-145								
39	44	-44	7	110	-110	1	147	-147	12	146	-146	3	58	-58	1	145	-145	6	51	-48	1	145	-145	6	51	-48	1	145	-145	6	51	-48	1	145	-145								
40	1	36	-37	9	142	-120	1	106	-111	7	44	-110	100	10	7	12	3	137	-128	6	54	-52	10	42	-56	1	155	-157	3	30	-32	1	147	-121									
41	2	467	471	6	53	58	1	101	-101	1	223	-242	12	26	-16	0	125	-127	4	276	-260	6	133	-139	1	266	-284	5	51	-47	6	40	-35	1	147	-121							
42	308	301	7	19	-14	3	47	-50	2	354	-354	13	151	-152	3	65	-69	7	204	-209	10	150	-151	4	217	-211	5	51	-47	6	40	-35	1	147	-121								
43	125	-169	3	40	-39	7	13	-16	12	118	-118	9	93	-97	1	207	-197	1	161	-167	4	216	-212	5	51	-47	6	40	-35														

gauche to the C(6)–C(7) bond. The C(6)–C(7)–C(9)–C(10) torsion angle is  $71^\circ$ . Consequently rings B and C approach each other quite closely with the C(10)…C(16) intramolecular distance only 3.23 Å.



A stereodiagram of the packing is shown in Fig. 3. While there seems to be a definite S…S intramolecular attraction there do not appear to be strong intermolecular S…S attractions, and closest S…S intermolecular distance is S(1)…S(1') at 3.72 Å. Other intermolecular separations, either close or to slightly less than van der Waals distances, are: S(8)…C(2) at 3.54, S(8)…N(4) at 3.63, N(4)…C(13) at 3.46, C(7)…C(23) at 3.44, and C(9)…C(23) at 3.47 Å.

### References

- BEER, R. J. S., FREW, D., JOHNSON, P. L. & PAUL, I. C. (1970). *Chem. Commun.* p. 154.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORFLS. Report ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- FLIPPEN, J. L. & KARLE, I. L. (1970). *J. Phys. Chem.* **74**, 769.
- GRASHEY, R., BAUMANN, M. & HAMPRECHT, R. (1970). *Tetrahedron Letters*, p. 5083.
- HORDVIK, A. (1968). *Acta Chem. Scand.* **22**, 2397.
- JOHNSON, P. L. & PAUL, I. C. (1969). *Chem. Commun.* p. 1014.
- JOHNSON, S. M., NEWTON, M. G. & PAUL, I. C. (1969). *J. Chem. Soc. (B)*, p. 986.
- KARLE, I. L., ESTLIN, J. A. & BRITTS, K. (1967). *Acta Cryst.* **22**, 273.
- KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* **16**, 969.

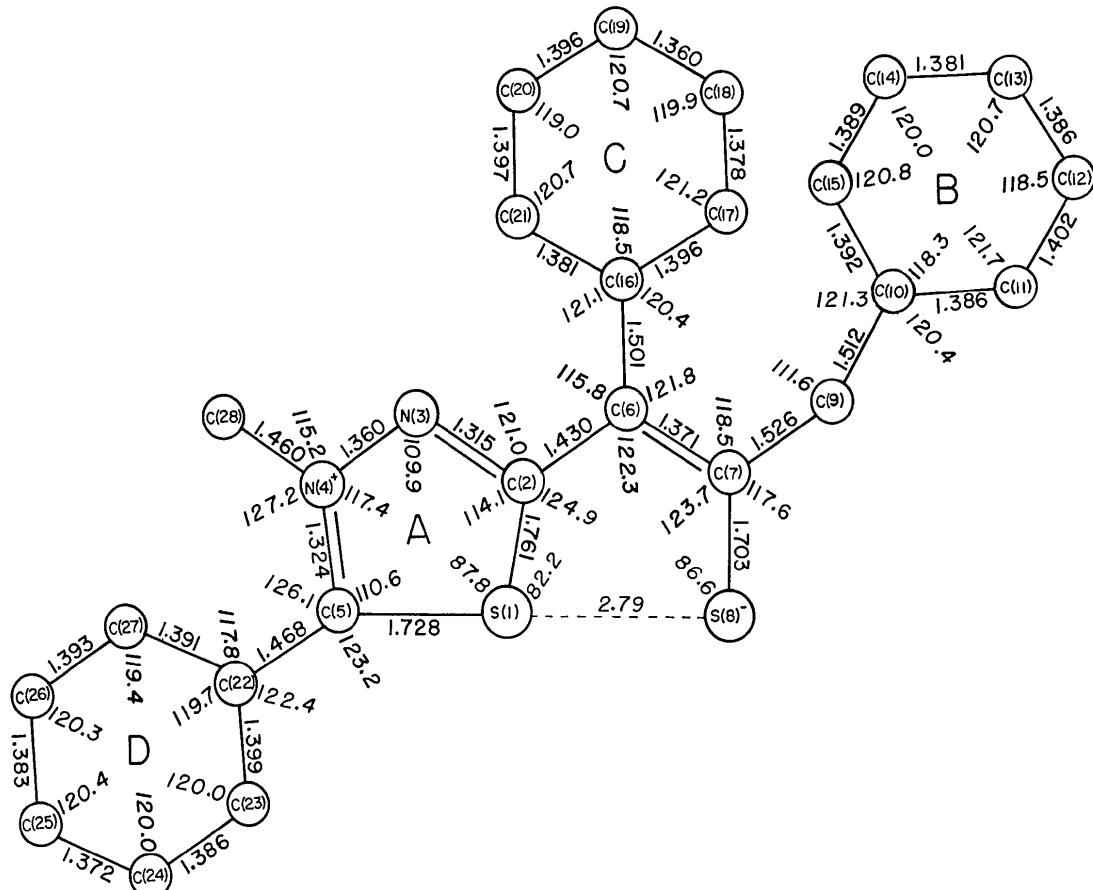


Fig. 2. Bond distances and angles for the thiadiazole derivative. Standard deviations estimated from the least-squares refinement are 0.004 Å for bonds involving S or N atoms, 0.008 Å for C–C bonds and 0.4° for the angles.

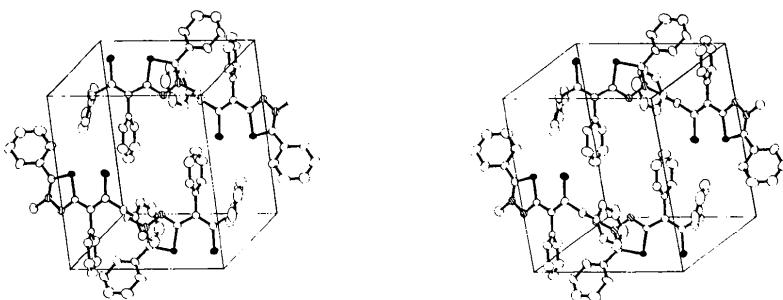


Fig. 3. Contents of one unit cell. The sulfur atoms are shown as  $\bullet$  and the nitrogen atoms as  $\circ$  ( $a$  is into the paper).

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.  
MORIARTY, R. M., MUKHERJEE, R., FLIPPEN, J. L. & KARLE,  
J. (1971). *Chem. Commun.* p. 1436.

PAULING, L. (1960). *The Nature of the Chemical Bond*.  
Cornell Univ. Press: Ithaca.  
SLETTEN, J. (1969). *Chem. Commun.* p. 688.

*Acta Cryst.* (1972). **B28**, 2754

## Crystal and Molecular Structure of *N-p*-Bromobenzoyl-*exo*-2,3-aziridinobicyclo[2,2,1]heptane\*

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*N-p*-Bromobenzoyl-*exo*-2,3-aziridinobicyclo[2,2,1]heptane,  $\text{BrC}_6\text{H}_4\text{CONC}_7\text{H}_{10}$ , crystallizes in the monoclinic space group  $P2_1/a$  with  $a = 12.43 \pm 0.01$ ,  $b = 17.13 \pm 0.02$ ,  $c = 6.08 \pm 0.01$  Å,  $\beta = 104.2 \pm 0.1^\circ$  and  $Z = 4$  (at 22°C). The structure was determined by the heavy-atom method using three-dimensional diffractometer data. The final  $R$  value for 1924 observed reflexions within the limits  $2\theta \leq 130^\circ$  with  $\text{Cu K}\alpha$  radiation is 5.2%. The three bond distances in the bicyclo[2,2,1]heptane system, C(1)–C(2), C(2)–C(3) and C(3)–C(4) with values of 1.497, 1.491 and 1.512 Å respectively, are shorter than the unstrained C–C single-bond distance. The bond angle C(1)–C(7)–C(4) in the same heptane system with a value of 95.4° is highly strained.

### Introduction

The addition of alkoxy carbonyl nitrenes to norbornylene has been assumed to give the corresponding alkoxy carbonyl aziridine (Scheiner, 1967; Ochlsehlager, McDaniel, Thakore, Tillman & Zalkow, 1969), as shown in Fig. 1(a). This conclusion was supported by the n.m.r. spectra of the products, which indicated apparent equivalence of the two hydrogens on the carbons attached to nitrogen (Tori, Kitahnoki, Takano, Tanida & Tsuji, 1965). However ring-opening reactions of the corresponding base gave 2,7-disubstituted norbornane derivatives (Edwards, Elder & Lesage, 1971; Tanida, Tsuji & Irie, 1966). Similarly the product of addition of *N*-benzenesulphonylnitrene to norbornylene gave 2,7-disubstituted derivatives on ring-open-

ing on the base (Ochlsehlager & Zalkow, 1963). These results suggested that the addition products were actually the azetidine derivatives [Fig. 1(b)]. Hence it seemed desirable to provide more conclusive proof of the structure of one of these adducts by X-ray analysis.

The adduct from light-induced addition of ethyl azidoformate to norbornylene was hydrolysed gently to the free base and this acylated with *p*-bromobenzoyl chloride yielded the compound of the present study.

### Experimental

Slow evaporation of a solution of the substance in benzene yielded small needle-like crystals elongated along the  $c$  axis. The crystals were colourless before exposure to the atmosphere, but developed a strong purple colour when exposed. The space-group symmetry and the initial lattice parameters were determined from precession photographs taken with the X-ray beam parallel to the  $a^*$  and  $b^*$  axes. The crystals be-

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