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The Crystal Structure of $C_{24}H_{20}N_2S_2$. A New Mesoionic Thiadiazole Derivative

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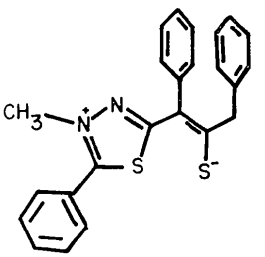
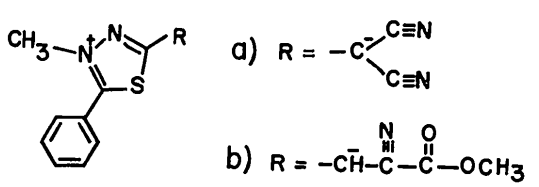
The stereochemistry of a new mesoionic thiadiazole derivative



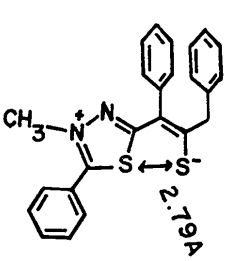
($C_{24}H_{20}N_2S_2$) has been established by X-ray analysis. The two sulfur atoms, which are in a *syn* conformation with respect to one another, are separated by only 2·79 Å. The material crystallizes in the monoclinic space group $P2_1/n$ with $a=14{\cdot}673$ (2), $b=11{\cdot}037$ (2), $c=12{\cdot}995$ (2) Å, $\beta=102{\cdot}1$ (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 $CH_2C_6H_5$ 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, Flippen & 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.



I



II

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 ($\sim 4\times 2{\cdot}5\times 1{\cdot}5$ mm) precluded its use for data collection. The 3325 X-ray data [maximum $(\sin\theta)/\lambda=0{\cdot}557$] were obtained [at room temperature on a four-circle computer controlled diffractometer using the θ–2θ technique with a $1{\cdot}8+2\theta(\alpha_2)$–$2\theta(\alpha_1)$ 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, $C_{24}H_{20}N_2S_2$, crystallizes in the monoclinic space group $P2_1/n$ with $a=14{\cdot}673$ (2), $b=11{\cdot}037$ (2), $c=12{\cdot}995$ (2) Å and $\beta=102{\cdot}1$ (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^{-3}. The absorption coefficient for this molecule is 29·46 cm^{-1}. The maximum μ_R is 1·5.

The structure was solved using the symbolic addition procedure for centrosymmetric crystals (Karle & Karle, 1963, 1966). The implementation of the $\sum_2$ 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 $1/w=(|F_o|/15)^2+1{\cdot}0$ 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

$$T=\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)\right].$$

The B_{ij}'s are in Å^2.

Standard deviations are based solely on least-squares parameters.

	X	Y	Z	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)	0.43458(15)	0.56443(23)	0.11689(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)	2.30(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)	2.39(10)	2.96(11)	2.99(11)	-0.28(8)	0.54(8)	0.01(8)
S(8)	0.42845(5)	0.78236(6)	-0.03356(5)	3.85(3)	3.13(3)	2.39(3)	-0.42(2)	0.12(2)	0.59(2)
C(9)	0.50222(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)	0.46088(23)	0.98435(28)	0.31739(25)	4.36(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)	8.40(24)	0.16(10)	2.03(15)	-0.13(14)
C(15)	0.33724(21)	0.94891(27)	0.16919(28)	3.44(12)	3.32(12)	5.49(16)	-0.15(9)	0.43(11)	-0.56(11)
C(16)	0.51724(19)	0.67689(22)	0.27468(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)	0.62(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(30)	10.82(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)	0.31485(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)	0.16487(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 (±0·2 A) with ring *A* planar to within ±0·02 Å. All three benzene rings are planar; ring *B* to within ±0·004 Å, ring *C* to within ±0·007 Å and ring *D* to within ±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 $F_c \times 10$.

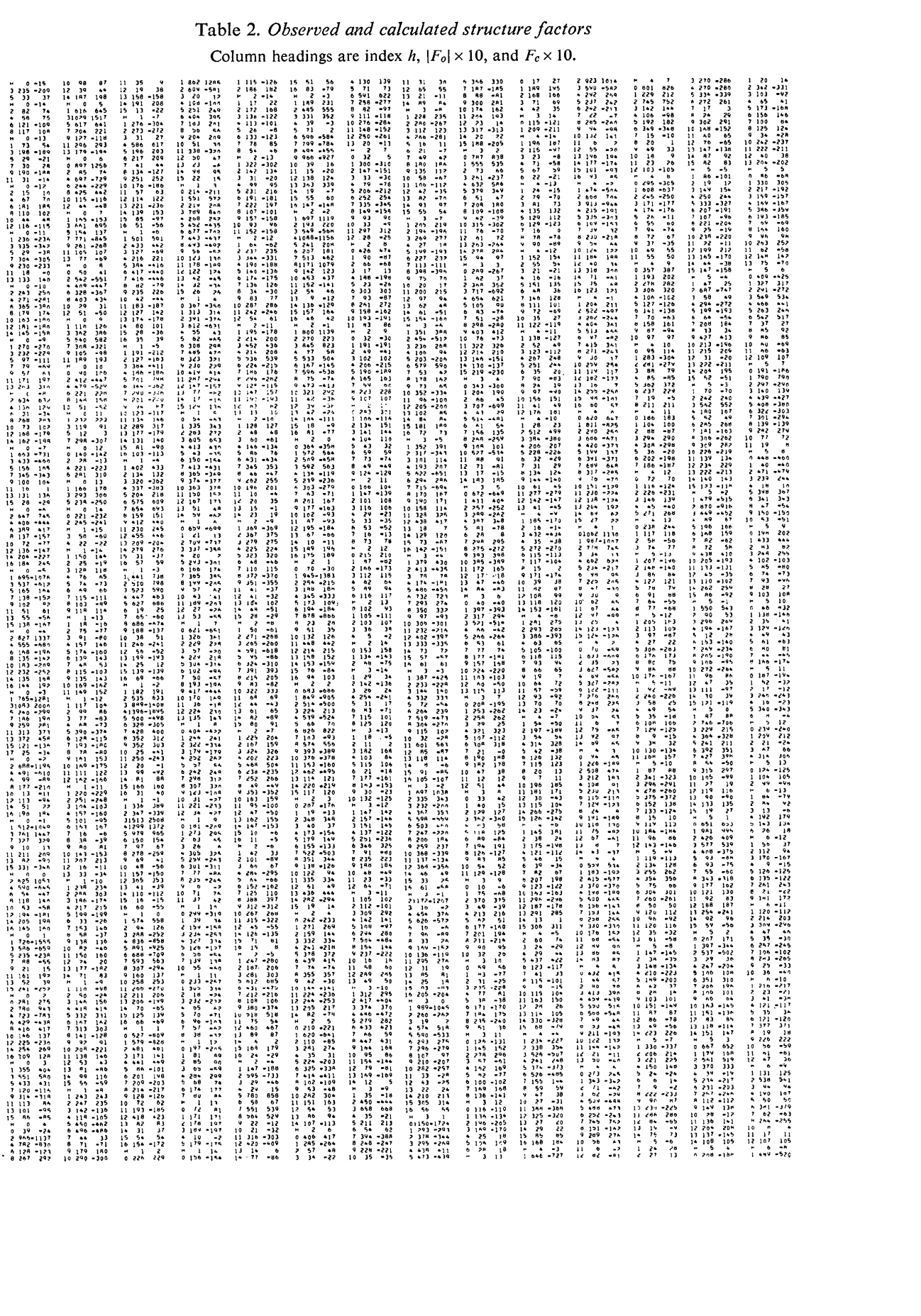


Table 2 (*cont.*)

atom and another sulfur or oxygen atom in the same molecule. In the present molecule (II) S(8) has a formal negative charge. The C(7)–S$^-$(8) distance of 1·703 Å is longer than that observed for 'unattracted' C=S bonds and also is 0·05 A longer than the C=S value in IV. However, it has the same value as the C=S distance in V in which the sulfur atom forms an additional 'long' bond of 2·48 Å to another sulfur atom. The conjugated system of bonds is similar in II and V. The C(9)–C(10) bond to which ring *B* is attached is

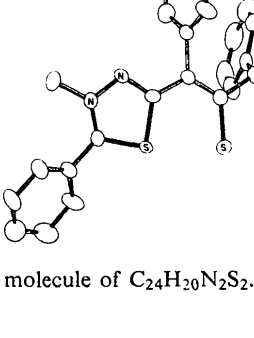
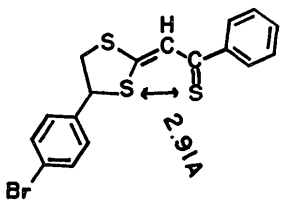
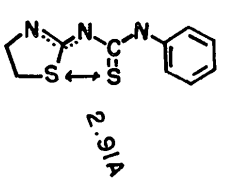


Fig. 1. Stereodiagram of a molecule of $C_{24}H_{20}N_2S_2$. The ellipsoids indicate the thermal motion at the 50% probability level.

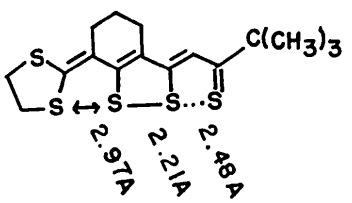
gauche to the C(6)–C(7) bond. The C(6)–C(7)–C(9)–C(10) torsion angle is 71°. Consequently rings *B* and *C* approach each other quite closely with the C(10)···C(16) intramolecular distance only 3·23 Å.



III



IV



V

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.

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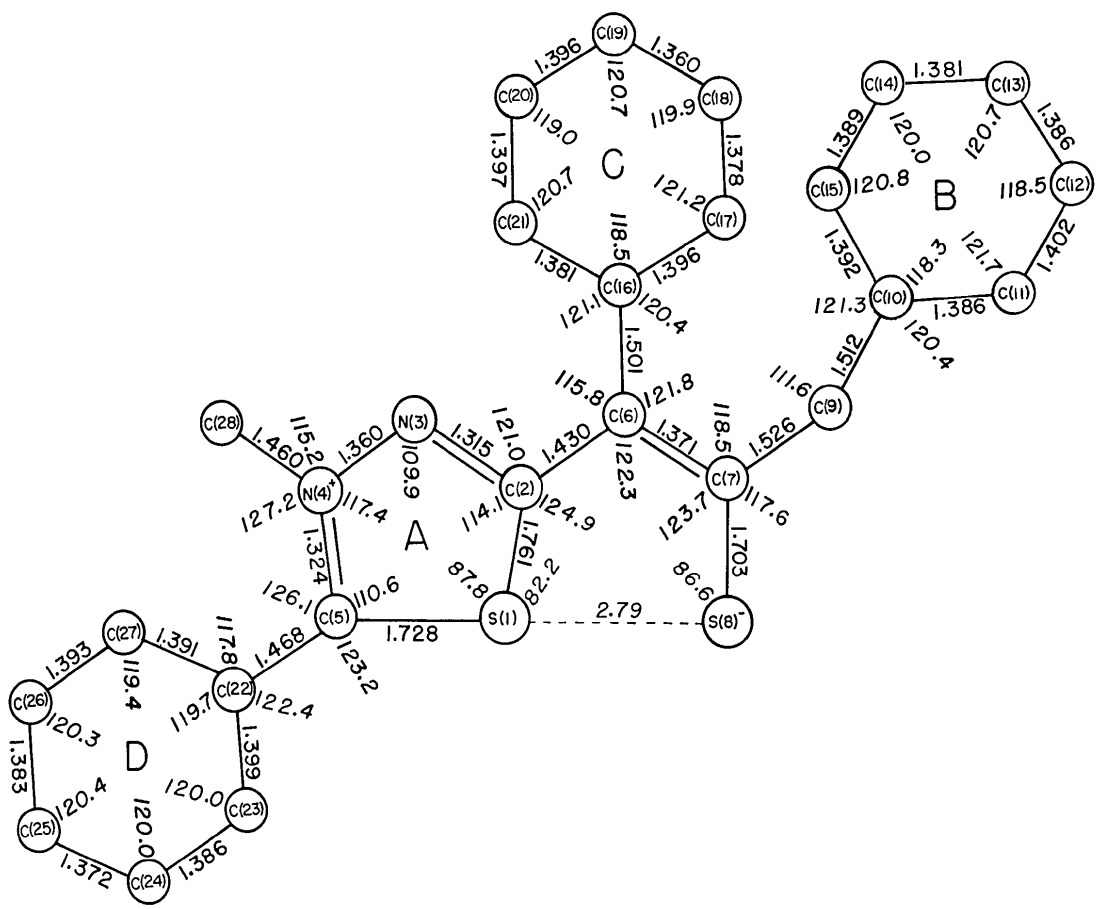

Fig. 2. Bond distances and angles for the thiadiazole derivative. Standard deviations estimated from the least-squares refinement are 0·004 Å for bonds involving S or N atoms, 0·008 Å for C–C bonds and 0·4° for the angles.

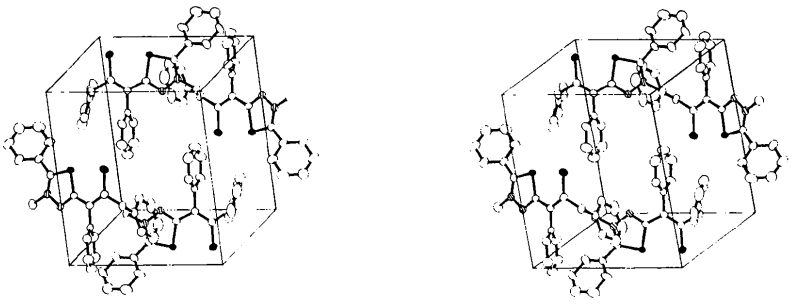

Fig. 3. Contents of one unit cell. The sulfur atoms are shown as ● and the nitrogen atoms as ◎ (**a** is into the paper).

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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, $BrC_6H_4CONC_7H_{10}$, crystallizes in the monoclinic space group $P2_1/a$ with $a=12{\cdot}43\pm0{\cdot}01$, $b=17{\cdot}13\pm0{\cdot}02$, $c=6{\cdot}08\pm0{\cdot}01$ Å, $\beta=104{\cdot}2\pm0{\cdot}1°$ 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 $2\theta\leq130°$ with 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 alkoxycarbonyl nitrenes to norbornylene has been assumed to give the corresponding alkoxycarbonylaziridine (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, Takono, 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*-benzenesulphoxylnitrene to norbornylene gave 2,7-disubstituted derivatives on ring-opening 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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