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The Crystal and Molecular Structure of a 2*H*-Thiopyran *p*-Bromobenzylester, $C_{20}H_{22}O_4NS_2Br$

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The structure and configuration of the isostructural 1:1 adducts of maleic anhydride with a series of *N*-substituted methyl 3-aminodithioacrylates have been determined from three-dimensional data collected on an automatic diffractometer using graphite monochromated Mo $K\alpha$ radiation. All attempts to determine their structure by both chemical and spectroscopic methods had been unsuccessful. Crystals of a bromine derivative $C_{20}H_{22}O_4NS_2Br$ were used for the structure determination by X-rays. The unit cell is monoclinic, space group $P2_1$ (C_2^2), $a=11{\cdot}36$ (1), $b=8{\cdot}052$ (5), $c=11{\cdot}77$ (1) Å, $\beta=99{\cdot}86$ (5)°, with two molecules of $C_{20}H_{22}O_4NS_2Br$ per unit cell. The observed and calculated densities are 1·52 (4) and 1·516 g.cm^{-3} respectively. The structure was determined by Patterson–Fourier methods and refined by the full-matrix least-squares technique to an R index on F of 0·057 for 1429 reflections. The X-ray results show that the adduct possesses the 2*H*-thiopyran structure. The structure determination led to the postulation of a previously undetermined mechanism for the reaction between maleic anhydride and *N*-substituted methyl 3-aminodithioacrylates.

Introduction

In the course of a study (Smutny, 1967) of the chemistry of the 3-dialkylaminodithioacrylates, a reactive group of compounds readily derived from the trithiones, the dithioacrylates shown in Fig. 1, were observed to undergo rapid (*ca.* 1 hr) reaction with maleic anhydride in benzene at ambient temperature to afford in high yield a series of isostructural 1:1 adducts. Although the infrared and n.m.r. spectra (Kalish, Smith & Smutny, 1971) of these adducts clearly show them to be unsaturated carboxylic acids, neither the spectral parameters nor the results of chemical degradation allowed assignment of a unique structure. Without knowledge of the structure of the adduct it had not been possible to write a reasonable mechanism for the reaction between maleic anhydride and *N*-substituted methyl 3-aminodithioacrylates (Kalish *et al.*, 1971). An X-ray structure determination of the adduct was therefore carried out. The adduct from the dithioacrylate Fig. 1(*b*) and maleic anhydride was converted to the corresponding *p*-bromobenzylester $C_{20}H_{22}O_4NS_2Br$ (Fig. 2), which was used for the structure determination.

Collection and reduction of the data

Difficulties were encountered in growing crystals of the 1:1 adduct ($C_{20}H_{22}O_4NS_2Br$) large enough for X-ray examination. By repeated recrystallization by slow cooling (8–9 days) of a sealed vial of warm (70°C) saturated solution of the Br compound in a cyclo-

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hexane–benzene mixture, crystals approximately 0·24 × 0·25 mm in cross section were finally obtained. Optical examination showed that all the crystals were twinned. Sections of crystals free of twins and satisfactory for structure determination were obtained by carefully cleaving the crystals under a microscope.

A series of precession and Weissenberg photographs taken with Ni-filtered Cu *K* radiation showed the crystals to be monoclinic with $2/m$ Laue symmetry. The only systematic extinctions observed were $0k0$ with k odd. These absences are consistent with space groups $P2_1$ (C_2^2) and $P2_1/m$ (C_{2h}^2). The unit-cell dimensions were measured on a Picker diffractometer using Zr-filtered Mo $K\alpha$ radiation. Twelve medium to high angle reflections were manually measured and used for a least-squares refinement of the parameters. The unit-cell dimensions at 18 °C were a = 11·36 (1), b = 8·05$_2$ (5), c = 11·77 (1) Å, β = 99·86 (5)° [λ(Mo $K\alpha$) = 0·71069 Å]. An approximate density of 1·52 ± 0·04 g.cm^{-3} was obtained by flotation in liquids of varying density, in good agreement with the calculated value of 1·516 g.cm^{-3} for two formula units of $C_{20}H_{22}O_4NS_2Br$ per unit cell. Space group $P2_1/m$ would require four molecules per unit cell for general positions, therefore the space group was taken as $P2_1$.

Intensity data were collected by the θ–2θ scan technique at a scan rate of 0·5° per min using graphite monochromated Mo $K\alpha$ radiation. The scan range was −1·00° from $K\alpha_1$, to +1·00° from the 2θ value calculated for $K\alpha_2$. Stationary-counter, stationary-crystal background counts of 20 sec were taken at each end of the scan range. The scintillation counter, which had an aperture of 6 × 7 mm, was 27 cm from the crystal. Calibrated molybdenum foil attenuators were inserted automatically when the intensity exceeded about 7000 counts per sec. Standard reflections were monitored every two hours. There were no variations in their intensity beyond that expected from counting statistics. Data were collected up to $2\theta \simeq 50°$; there were very few reflections above background beyond $2\theta \simeq 45°$. The data were corrected for Lorentz and polarization effects for the monochromator (Smith, 1972) but not for absorption, since the primary object was to determine the general structure of the molecule. The dimensions of the crystal, which was approximately a rectangular prism, were 0·244 × 0·120 × 0·340 mm. The linear absorption coefficient for Mo $K\alpha$ is 22·39 cm^{-1}, μR for the crystal ranged from 0·134 to 0·382 with maximum range in transmission factors for I of 0·43 to 0·76.

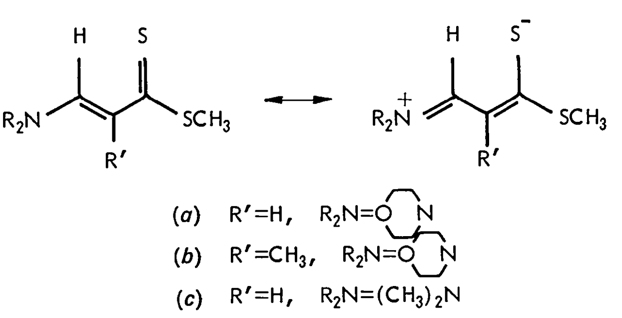

Fig. 1. Dithioacrylates.

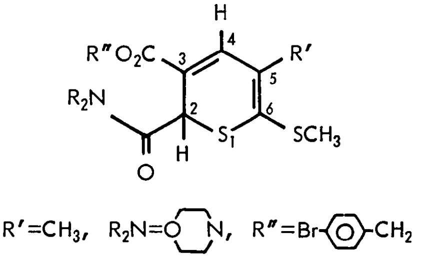

Fig. 2. p-Bromobenzylester $C_{20}H_{22}O_4NS_2Br$ used for the structure determination.

The weighting scheme and expression for the intensity (I) were similar to those of Busing & Levy (1957) and that of Corfield, Doedens & Ibers (1967) with p = 0·02. Of the 1420 reflections collected, 1295 with $I \geq 3\sigma(I)$ were given $w > 0$. $\sigma(F)$ was taken equal to

$$\sigma(F) = \frac{[S_1\sigma(F_o)^2]^{1/2}}{2F_o}$$

where S_1 is a scale factor.

Structure determination

The structure was solved by interpretation of a series of 3-dimensional Patterson functions, Fourier and difference-Fourier syntheses and least-squares calculations. The Br coordinates were determined from a 3-dimensional Patterson function.* The sulfur atoms were located on the interpretation of a combination of the 3-dimensional Patterson function, the Fourier syntheses phased on the Br atom, and the ($h0l$) projection which is centrosymmetric in this space group. All the other atoms were located successively from a series of Fourier syntheses and difference-Fourier syntheses interspersed with least-squares calculations, using the identified atoms to calculate the successive Fourier syntheses. After all the atoms except hydrogen had been located, two cycles of full-matrix least squares were computed using anisotropic temperature factors for the Br and S atoms and isotropic temperature factors for the other atoms. The R value:

$$R = \frac{\sum ||F_o| - |F_c||}{\sum F_o}$$

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* In addition to various local programs, the following programs were used: Busing and Levy's *ORFLS* program, Zalkin's *FORDAP* Fourier, *ISLONG* least-squares, *DISTAN* distance and angle programs, and Johnson's ORTEP thermal ellipsoid program. Hope's program *HPOSN* was used to calculate the hydrogen positions.

Table 1. *Thermal parameters*

The standard deviation of the least significant figure is given in parentheses. Anisotropic thermal parameters are in the form $\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{13}+2hl\beta_{13}+2kl\beta_{23})\right]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	5·79 (8)	4·65 (8)	9·95 (14)	1·97 (8)	−1·07 (8)	−0·22 (11)
S(1)	4·30 (17)	3·92 (17)	5·36 (24)	−1·82 (14)	2·01 (16)	−1·05 (17)
S(2)	6·67 (25)	6·68 (27)	7·74 (35)	−0·56 (21)	4·98 (23)	0·69 (24)
C(1)	4·5 (8)	4·1 (8)	4·6 (9)	0·5 (6)	−1·2 (6)	−0·4 (7)
C(2)	4·7 (7)	3·7 (7)	6·3 (10)	0·8 (6)	1·9 (7)	0·5 (7)
C(3)	3·9 (7)	3·4 (7)	6·9 (11)	0·2 (6)	2·3 (7)	0·8 (7)
C(4)	3·8 (6)	3·5 (6)	3·6 (8)	0·6 (6)	1·2 (5)	−0·7 (8)
C(5)	3·9 (6)	4·7 (9)	5·4 (9)	0·6 (6)	1·3 (6)	0·5 (7)
C(6)	3·9 (7)	5·3 (8)	6·7 (11)	1·3 (6)	1·9 (7)	0·1 (8)
C(7)	4·6 (7)	3·1 (7)	5·6 (11)	−0·2 (6)	1·5 (7)	0·3 (7)
C(12)	2·7 (6)	6·5 (10)	4·7 (10)	−1·2 (6)	1·7 (6)	−1·7 (8)
C(13)	5·4 (8)	5·7 (9)	5·5 (11)	1·4 (7)	2·8 (7)	−0·7 (8)
C(14)	9·1 (12)	6·0 (10)	7·7 (12)	0·7 (9)	2·8 (9)	1·2 (9)
C(17)	5·6 (8)	3·8 (9)	3·9 (9)	−0·5 (6)	0·1 (6)	−1·0 (6)
C(18)	5·2 (8)	3·6 (7)	4·7 (10)	−0·9 (6)	−0·3 (7)	0·3 (7)
C(19)	6·0 (8)	5·1 (9)	5·0 (10)	−0·7 (7)	0·0 (7)	1·1 (8)
C(20)	3·6 (7)	4·3 (7)	5·6 (10)	0·2 (5)	−0·9 (6)	0·3 (7)
O(1)	5·2 (4)	4·0 (4)	3·5 (5)	0·7 (4)	2·4 (4)	0·5 (4)
O(2)	4·3 (4)	4·8 (6)	5·3 (5)	0·5 (4)	2·6 (4)	−0·1 (5)
O(3)	7·2 (7)	3·9 (5)	6·1 (8)	0·8 (5)	0·2 (6)	0·8 (5)
O(4)	3·6 (4)	3·8 (4)	4·0 (5)	−0·3 (4)	0·6 (3)	0·1 (4)
N	4·6 (6)	2·9 (5)	4·0 (7)	0·4 (4)	0·1 (5)	0·0 (5)

	B*
C(8)	3·4 (3)
C(9)	3·0 (2)
C(10)	3·1 (3)
C(11)	3·6 (3)
C(15)	3·6 (3)
C(16)	3·0 (2)

* B is the isotropic thermal parameter in Å^2.

dropped from 0·17 to 0·08 for 1295 reflections. The approximate coordinates of all 20 hydrogen atoms were located at this stage by a difference-Fourier synthesis. The methyl hydrogens were quite diffuse; therefore only sixteen hydrogens at the theoretical calculated positions were included in the subsequent refinement. Three additional cycles of full-matrix least squares were carried out (233 parameters) with anisotropic temperature factors on the Br, S, N, O and 14 of the 20 carbon atoms that previous least-squares calculations indicated had the largest amplitude of thermal motion (Table 1). Isotropic temperature factors were assigned to the other six carbon atoms (Table 1) and to the hydrogen atoms; the latter were not varied during the least-squares calculations. The discrepancy index, R, decreased to 0·050 for 1295 reflections of non-zero weight and to 0·057 for 1429 reflections, R_w= 0·051. The standard deviation of unit weight was 1·021, close to the expected value of unity. No parameter shifted by more than $\frac{1}{10}$ of its estimated standard deviation. The positional and thermal parameters derived from the last cycle of least squares are presented in Tables 1 and 2 along with the associated standard deviations in these parameters estimated from the inverse of the normal equations matrix. The final values of F_o and F_c (in electrons) are given in Table 3 for the 1429 reflections used in the refinement.

Table 2. *Atomic coordinates*

The standard deviation of the least significant figure is given in parentheses.

	x	y	z
Br	0·0735 (1)	0·2500 (0)	0·3171 (2)
S(1)	0·1909 (3)	−0·0007 (5)	0·7270 (4)
S(2)	0·0817 (4)	0·0668 (6)	0·9310 (5)
C(1)	0·1490 (13)	0·0493 (19)	0·3537 (14)
C(2)	0·2527 (13)	0·0152 (19)	0·3089 (14)
C(3)	0·3071 (12)	0·8676 (18)	0·3372 (15)
C(4)	0·2637 (10)	0·7550 (22)	0·4042 (11)
C(5)	0·1600 (11)	0·7903 (19)	0·4448 (13)
C(6)	0·1039 (13)	0·9419 (22)	0·4191 (16)
C(7)	0·3291 (12)	0·5945 (18)	0·4325 (15)
C(8)	0·3230 (12)	0·3579 (17)	0·5475 (12)
C(9)	0·2725 (9)	0·2849 (15)	0·6428 (10)
C(10)	0·2054 (10)	0·3752 (15)	0·7063 (12)
C(11)	0·1631 (12)	0·3149 (19)	0·8050 (14)
C(12)	0·1533 (12)	0·1482 (22)	0·8241 (14)
C(13)	0·1231 (14)	0·4437 (21)	0·8865 (15)
C(14)	0·1814 (18)	0·9073 (24)	0·9942 (18)
C(15)	0·3106 (11)	0·1085 (16)	0·6722 (12)
C(16)	0·4275 (10)	0·1022 (17)	0·7548 (12)
C(17)	0·4462 (12)	0·7979 (17)	0·7231 (13)
C(18)	0·4470 (14)	0·6651 (19)	0·8143 (15)
C(19)	0·5768 (14)	0·8150 (22)	0·9474 (15)
C(20)	0·5901 (12)	0·9497 (19)	0·8657 (14)
O(1)	0·2863 (8)	0·5137 (12)	0·5250 (8)
O(2)	0·3899 (7)	0·2855 (12)	0·4968 (8)
O(3)	0·5529 (11)	0·6602 (14)	0·8905 (11)
O(4)	0·4697 (7)	0·2326 (12)	0·7952 (8)
N	0·4826 (10)	0·9565 (13)	0·7781 (10)

The quantity minimized in the least-squares calculations was $\sum w||F_o|-|F_c||^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes; the weights, w, were taken equal to the reciprocals of the variances $\sigma^2(F_o)$. The atomic scattering factors were taken from Cromer & Waber (1965) with the exception of those for hydrogen, which were taken from the Stewart, Davidson & Simpson (1965) values. The anomalous scattering factors for Br, S, O, N and C were applied throughout the refinement. Cromer's (1965) values for $\Delta f'$ and $\Delta f''$ were used.

Description of the structure

The X-ray structure determination showed that the 1:1 adduct possesses the 2*H*-thiopyran structure, Fig. 2. The structure of the molecule is shown in Fig. 3, in which the bond distances are listed, and in Fig. 4 and 5, which show the packing arrangement of the molecules in the unit cell projected along the *b* and *a* axes, respectively. The orientations of the thermal ellipsoids are indicated in the *ORTEP* (Johnson, 1965) stereoscopic drawing, Fig. 6. The principal interatomic dis-

Table 3. *Observed and calculated structure factors for* $C_{20}H_{22}O_4NS_2Br$ [*FCA*(000)=499·2]

```
FCA(0,0,0) = 499.20

   H FOB FCA
K,L=  0,   0
   1  10   7
   2   3   7
   3  55  48
   4  31  30
   5  41  39
   6  31  30
   7   8  10
   8  42  42
   9  14  14
  10   4   4*
  11   9   9
K,L=  0,   1
   0  43  55
   1  15   9
   2  53  48
   3  89  86
   4  91  87
   5   6   3
   6  15  15
   7  32  32
   8   4   3*
   9  14  14
  10   3   2*
  11  12  12
K,L=  0,   2
   0  60  66
   1  45  43
   2  67  70
   3 109 109
   4  21  21
   5   8   8
   6   4   3
   7  14  13
   8   8  10
   9   6   5
  10  12  12
  11  17  16
K,L=  0,   3
   0  43  43
   1  41  41
   2  15  15
   3   8   9
   4  82  81
   5  22  22
   6  21  20
   7  47  48
   8  23  23
   9   6   7
K,L=  0,   4
   0  17  18
   1  29  29
   2   3   4
   3  58  58
   4   6   6
   5   8   7
   6  21  20
   7  14  13
   8   4   3*
   9   4   2*
  10  17  14
K,L=  0,   5
   0  51  52
   1   7   5
   2  10  11
   3   5   5
   4  18  18
   5  16  17
   6  33  33
   7  24  23
   8   9   9
   9  10   8
  10  12  10
K,L=  0,   6
   0  18  17
   1  11  10
   2   3   3*
   3  44  44
   4   0   2*
   5   6   7
   6  11  11
   7   8   7
   8   8   7
   9   7   7
  10  11  10
K,L=  0,   7
   0   0   2*
   1  10  11
   2  35  35
   3  23  23
   4  12  12
   5   4   3*
   6  11  12
   7   5   2
   8   4   2*
   9  12  11
K,L=  0,   8
   0  23  22
   1  20  20
   2   7   6
   3   1   1*
   4   8   9
   5  11   9
   6  13  12
   7  15  14
   8   8   7
K,L=  1,   0
   1  80  74
   2  79  74
   3  89  83
   4  36  37
   5  35  34
   6   9  10
   7  15  14
   8  12  11
   9  19  17
  10  17  17
K,L=  1,   1
   0  26  34
   1  48  43
   2  74  72
   3  12  13
   4  42  43
   5  15  15
   6  56  56
   7  26  27
   8  13  14
   9   5   5
  10  13  14
K,L=  1,   2
   0  37  37
   1 116 118
   2 118 117
   3  23  25
   4  14  16
   5  10   9
   6  21  19
   7  25  25
   8  14  15
   9  16  15
  10  13  14
K,L=  1,   3
   0  41  41
   1  51  47
   2  53  54
   3  35  37
   4  49  49
   5  53  52
   6  21  20
   7  10   9
   8   8   9
   9  12  12
  10   8   9
K,L=  1,   4
   0  69  72
   1  27  30
   2  13  12
   3  14  15
   4  18  18
   5  24  24
   6  15  18
   7  16  17
   8  15  15
   9   9  10
  10   9   8
K,L=  1,   5
   0  36  36
   1  46  46
   2  31  32
   3  34  37
   4  12  12
   5  17  16
   6   7   7
   7  20  19
   8  15  15
   9  13  12
  10   9   7
K,L=  1,   6
   0  27  26
   1  17  16
   2  10  10
   3  20  21
   4  13  14
   5  18  17
   6  18  18
   7   4   4*
   8   3   2*
   9   6   4
  10   7   7
K,L=  1,   7
   0  17  15
   1   6   5
   2  19  19
   3  11  12
   4   2   4*
   5  10  10
   6  15  15
   7   9  10
   8   9   8
   9   7   7
K,L=  1,   8
   0  13  14
   1  16  15
   2  19  19
   3   9   8
   4  13  12
   5  12   9
   6   5   2
   7   1   1*
   8   6   4
K,L=  2,   0
   0  28  30
   1   7   4
   2  70  66
   3  20  19
   4   9   8
   5  20  20
   6  31  30
   7  12  13
   8  11  10
   9  13  11
  10  18  18
K,L=  2,   1
   0  38  40
   1  63  62
   2  81  78
   3  45  44
   4  18  17
   5  16  15
   6  20  20
   7  15  14
   8  14  14
   9  33  33
  10  12  12
K,L=  2,   2
   0  26  23
   1  30  31
   2  22  22
   3   6   5
   4  16  16
   5  57  57
   6  39  38
   7  20  20
   8   8   8
   9   9  10
  10   9   7
K,L=  2,   3
   0  25  26
   1  32  32
   2  47  45
   3  33  32
   4   7   6
   5  38  38
   6  21  20
   7  13  12
   8  17  16
   9  19  18
K,L=  2,   4
   0  21  21
   1  31  32
   2  19  19
   3  51  52
   4  50  50
   5  18  18
   6  15  15
   7   5   5
   8  21  21
   9  17  21
K,L=  2,   5
   0   3   0*
   1  35  35
   2  32  33
   3  13  12
   4  39  39
   5  22  21
   6  18  19
   7  16  16
   8   7   6
   9   6   6
K,L=  2,   6
   0  36  37
   1  43  43
   2  41  42
   3   5   3
   4   8   8
   5   8   8
   6   9  11
   7  12  11
   8  11  11
   9   8   7
K,L=  2,   7
   0  14  14
   1   7   7
   2   4   2*
   3  17  16
   4  21  22
   5  20  19
   6   8   6
   7   0   3*
   8   4   3*
   9   8   8
K,L=  2,   8
   0  19  19
   1  13  13
   2  11  12
   3  19  18
   4  13  13
   5   7   6
   6   3   3*
   7   2   2*
   8   7   6
K,L=  3,   0
   1  26  28
   2  28  29
   3  30  29
   4  34  33
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K,L=  3,   1
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K,L=  3,   3
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K,L=  3,   4
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K,L=  3,   5
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K,L=  3,   6
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   9   7   4
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K,L=  6,   2
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K,L=  6,   3
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K,L=  6,   6
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K,L=  7,   3
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K,L=  7,   4
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K,L=  7,   5
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K,L=  8,   1
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K,L=  0,   2
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K,L=  0,   3
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K,L=  1,   8
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K,L=  2,   5
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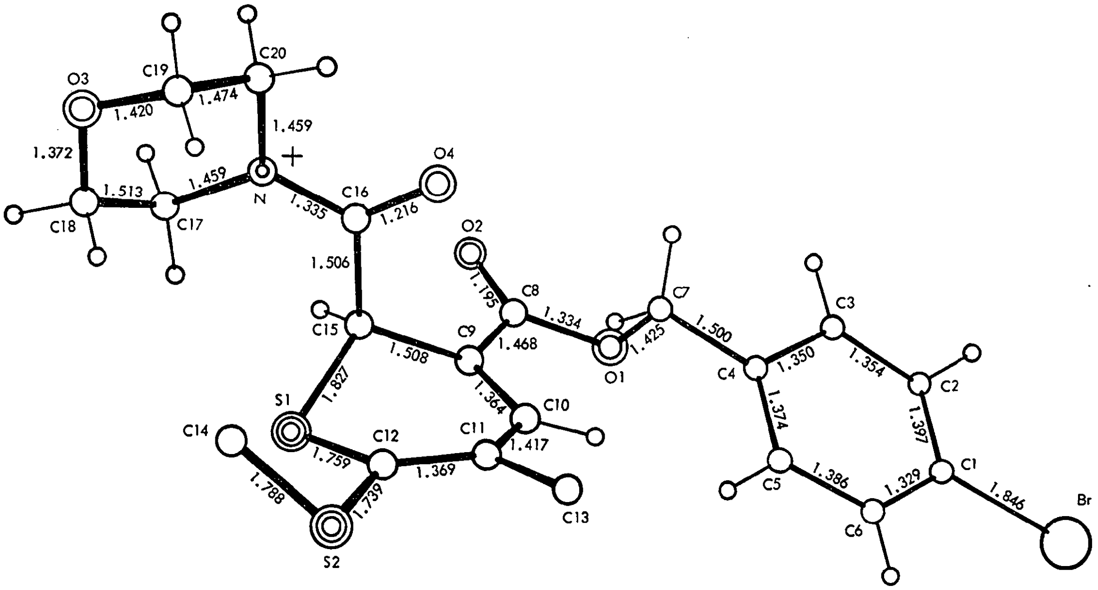

Fig.3. Structure of $C_{20}H_{22}O_4NS_2Br$ molecule, showing bond distances.

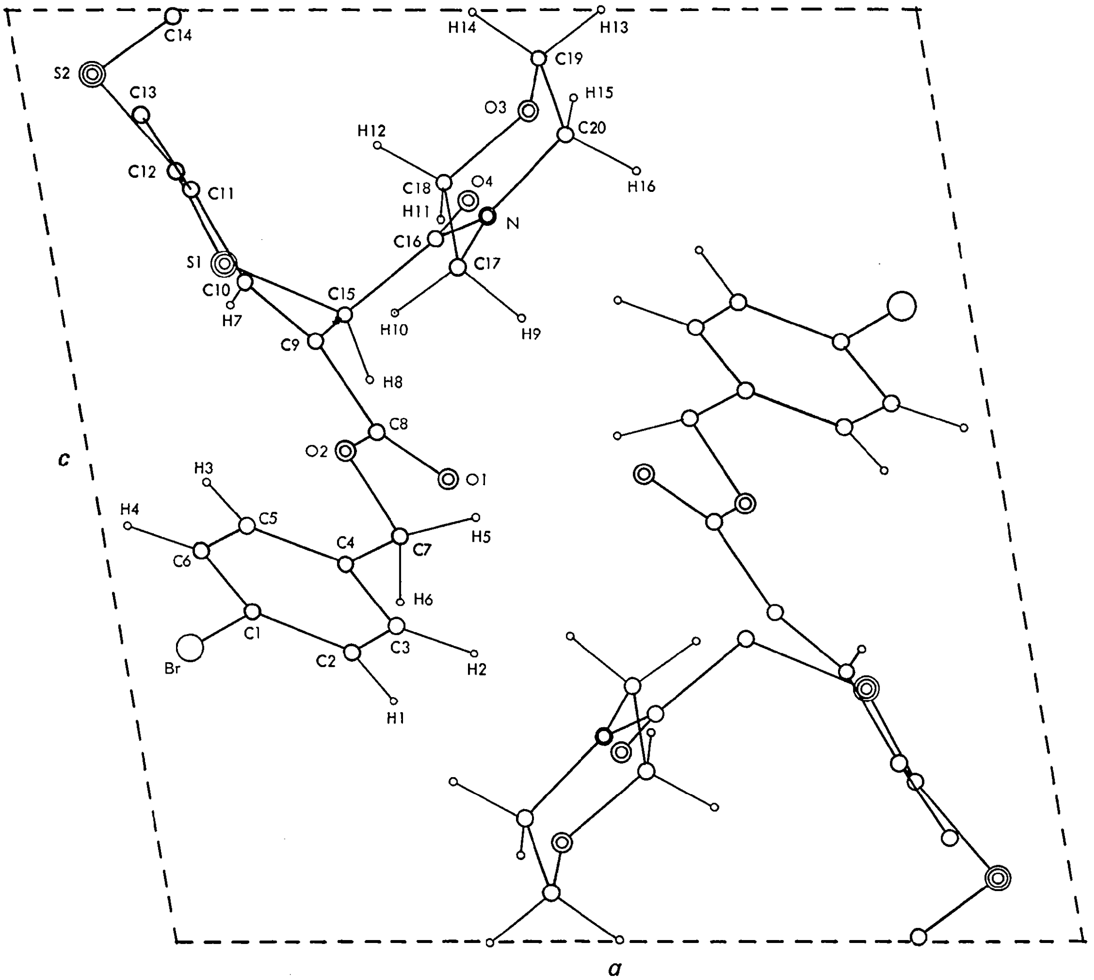

Fig.4. Unit cell of $C_{20}H_{22}O_4NS_2Br$, viewed along the *b* axis.

tances and angles and their standard deviations computed from the final parameters and the correlation matrix are presented in Tables 4 and 5. The standard deviations in bond lengths range from 0·017 to 0·023 Å for C–C bonds, from 0·016 to 0·021 Å for C–O bonds and from 0·017 to 0·018 Å for C–N bonds. The bond distances and bond angles are normal within the limit of experimental error, with the possible exception of C(1)–C(6). The apparent shortness of this bond may be related to the proximity of the Br atom, which is undergoing rather large anisotropic thermal motion. Since the thiopyran ring is the most interesting feature of the structure of the adduct, the bond distances and angles are given separately in Table 6. Carbon–carbon bonds C(11)–C(12) and C(9)–C(10), 1·364 (17) and 1·369 (23) Å respectively, are double bonds. This was confirmed by the difference Fourier syntheses, which showed there were no hydrogen atoms attached (Fig. 7) to carbon atoms C(9), C(11) and C(12), and by examination of the bond angles. The approximate planarity of atoms S(1), S(2), C(11), C(12) and C(13), and of atoms C(8), C(9), C(10), C(15) and H(7) and the fact that

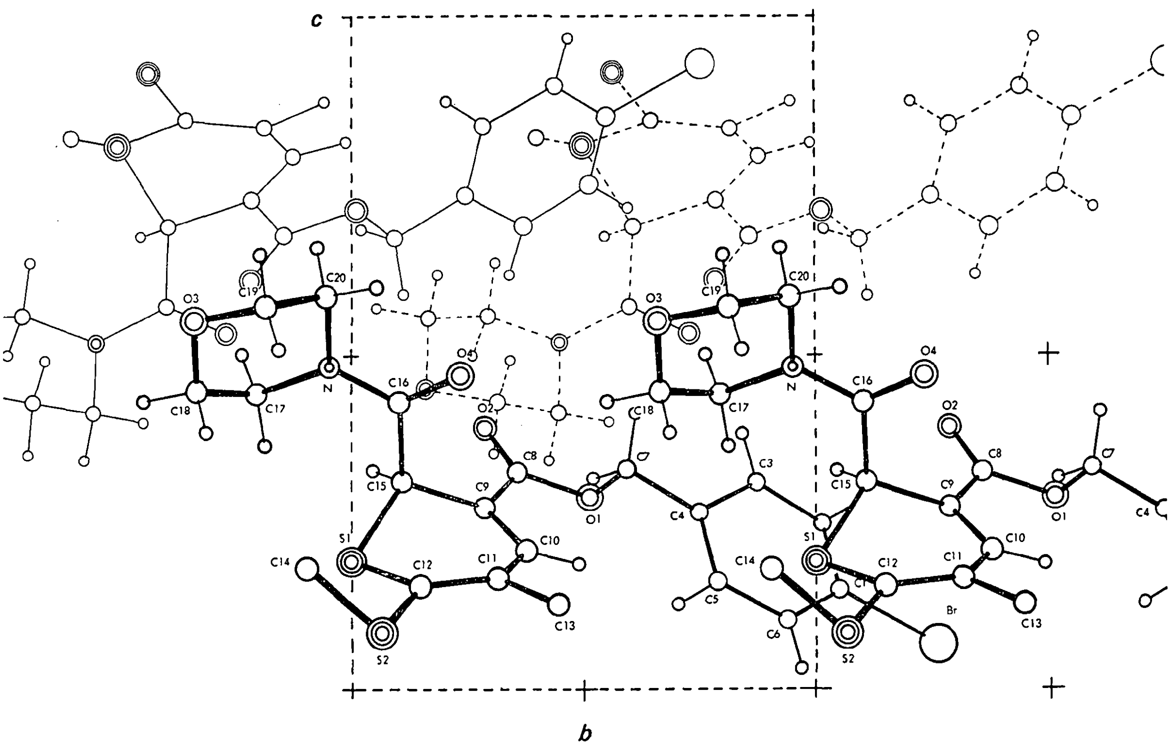

Fig. 5. Unit cell of $C_{20}H_{22}O_4NS_2Br$, viewed along the *a* axis.

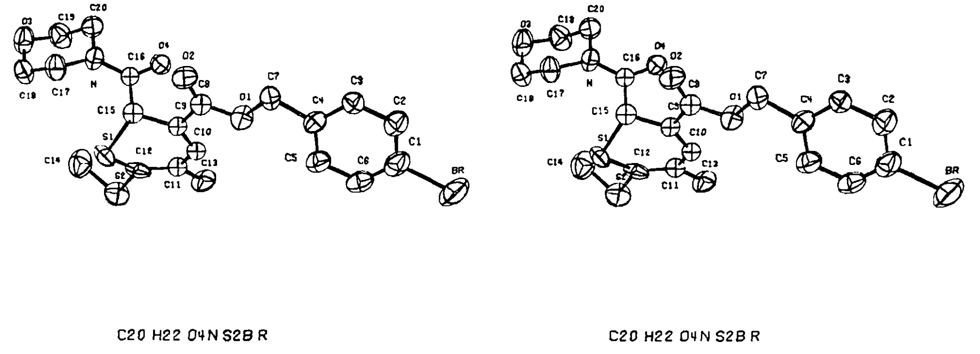

Fig. 6. *ORTEP* stereoscopic drawing of $C_{20}H_{22}O_4NS_2Br$ showing 50% probability ellipsoids For clarity, hydrogen atoms are omitted.

all the bond angles C(10)–C(9)–C(8), C(10)–C(9)–C(15), C(9)–C(10)–C(11), C(9)–C(10)–H(7), C(10)–C(11)–C(12), C(10)–C(11)–C(13), S(1)–C(12)–C(11) and S(2)–C(12)–C(11) are all close to 120°, indicate sp^2 bonding for carbon atoms C(9), C(10), C(11) and C(12). The equation of the least-squares plane through S(1), S(2), C(12), C(11) and C(13) based on monoclinic coordinates is $0{\cdot}82852X-0{\cdot}03337Y+0{\cdot}040883Z+5{\cdot}2932=0$. The deviations of the above atoms from this plane range from 0·002 to 0·075 Å. The equation of the least-squares plane through C(8), C(9), C(10), C(11), C(15) and H(7) in monoclinic coordinates is

$$0{\cdot}73366X+0{\cdot}30400Y+0{\cdot}47311Z+6{\cdot}5896=0\,.$$

The deviation of the atoms from this plane range from 0·005 to 0·041 Å. The non-planarity of the thiopyran ring is evident from Fig. 4. The S(1)–C(15) bond is normal but S(1)–C(12) and S(2)–C(12) are partial double bonds. Similar results for the corresponding S–C bonds were reported by Haque & Caughlan (1967). The bond distances and angles in the thiopyran ring are in agreement within the respective limits of error with those of Haque & Caughlan (1967).

Table 4. *Interatomic distances* (Å)

The standard deviation of the least significant figure is given in parentheses.

Br—C(1)	1·846 (15)	C(9)—C(10)	1·364 (17)
S(1)—C(15)	1·827 (13)	C(10)–C(11)	1·417 (20)
S(1)—C(12)	1·759 (17)	C(11)–C(12)	1·369 (23)
S(2)—C(12)	1·739 (17)	C(11)–C(13)	1·534 (23)
S(2)—C(14)	1·788 (20)	C(9)—C(15)	1·509 (18)
C(1)–C(2)	1·397 (21)	C(15)–C(16)	1·506 (18)
C(2)–C(3)	1·354 (21)	C(16)–O(4)	1·216 (16)
C(3)–C(4)	1·350 (22)	C(16)–N	1·335 (17)
C(4)–C(5)	1·374 (18)	C(17)–N	1·459 (18)
C(5)–C(6)	1·386 (23)	C(20)–N	1·459 (18)
C(6)–C(1)	1·329 (24)	C(17)–C(18)	1·513 (22)
C(4)–C(7)	1·500 (22)	C(18)–O(3)	1·372 (20)
C(7)–O(1)	1·425 (19)	C(19)–O(3)	1·420 (21)
C(8)–O(1)	1·334 (17)	C(19)–C(20)	1·474 (18)
C(8)–O(2)	1·195 (16)		
C(8)–C(9)	1·468 (18)		

The structure of the molecule as determined by X-rays, in particular the formation of the six-membered 2*H*-thiopyran ring, lead to the postulation of a previously undetermined reasonable mechanism of reaction between maleic anhydride and *N*-substituted methyl 3-aminodithioacrylates (Kalish *et al.*, 1971).

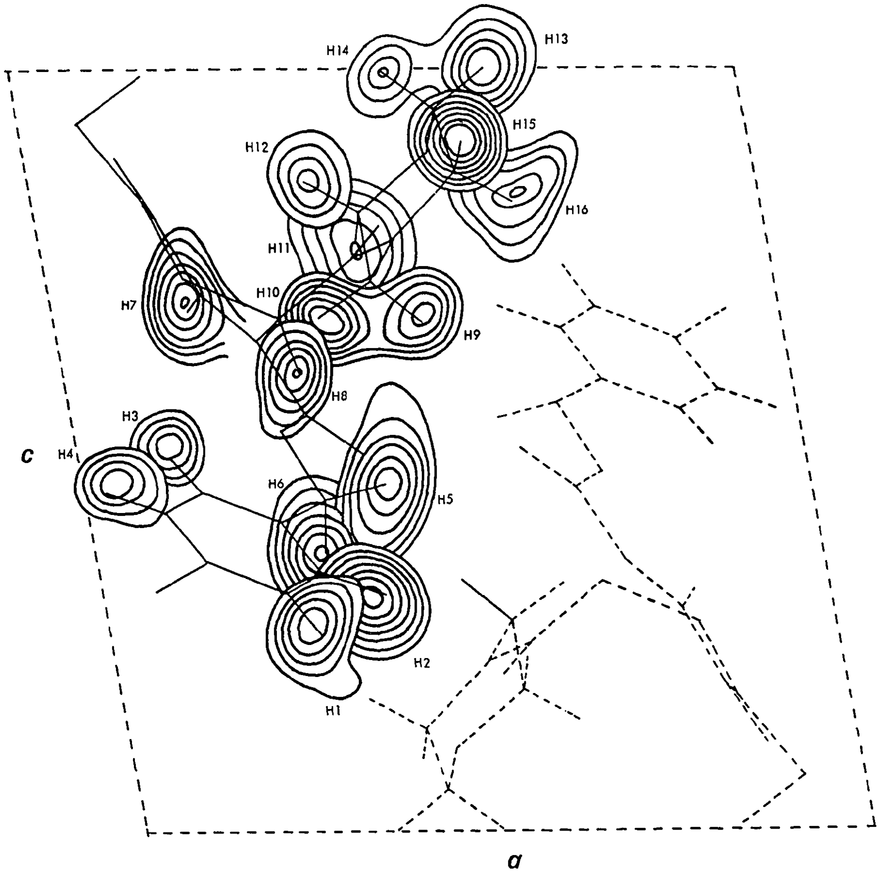

Fig. 7. Composite sections of a difference map indicating the location of hydrogen atoms. The contours are evenly spaced on an arbitrary scale.

Table 5. *Bond angles* (°)

The standard deviation of the least significant figure is given in parentheses.

Br—C(1)—C(2)	118·2 (1·2)	C(10)-C(9)—C(15)	122·8 (1·1)
Br—C(1)—C(6)	119·9 (1·2)	C(10)-C(11)-C(12)	121·3 (1·4)
C(1)-C(2)—C(3)	117·2 (1·4)	C(10)-C(11)-C(13)	117·4 (1·3)
C(2)-C(3)—C(4)	122·4 (1·4)	C(11)-C(10)-H(7)	120·0 (2·0)
C(3)-C(4)—C(5)	119·0 (1·5)	C(11)-C(12)-S(1)	121·7 (1·2)
C(4)-C(5)—C(6)	119·7 (1·4)	C(11)-C(12)-S(2)	123·4 (1·3)
C(2)-C(1)—C(6)	121·9 (1·5)	S(1) —C(12)-S(2)	114·2 (1·0)
C(3)-C(4)—C(7)	119·5 (1·2)	C(12)-S(2) —C(14)	103·4 (0·9)
C(5)-C(4)—C(7)	121·5 (1·4)	C(12)-S(1) —C(15)	100·4 (0·7)
C(4)-C(7)—O(1)	110·0 (1·1)	C(12)-O(11)-C(13)	121·2 (1·4)
C(7)-O(1)—C(8)	116·4 (1·0)	C(15)-C(16)-O(4)	117·9 (1·2)
O(1)-C(8)—O(2)	124·3 (1·3)	C(15)-C(16)-N	119·5 (1·2)
O(1)-C(8)—C(9)	112·2 (1·1)	O(4)—C(16)-N	122·6 (1·2)
C(8)-C(9)—C(10)	122·2 (1·1)	C(16)-N——C(17)	126·2 (1·1)
C(8)-C(9)—C(15)	114·7 (1·0)	C(16)-N——C(20)	119·0 (1·1)
C(9)-C(10)-C(11)	124·5 (1·2)	N——C(17)-C(18)	109·7 (1·2)
C(9)-C(15)-C(16)	111·5 (1·1)	N——C(20)-C(19)	108·8 (1·2)
C(9)-C(15)-S(1)	109·4 (0·8)	C(17)-C(18)-O(3)	112·4 (1·2)
C(9)-C(10)-H(7)	120·0 (2·0)	C(18)-O(3)—C(19)	111·0 (1·2)
		O(3)—C(19)-C(20)	111·7 (1·4)

Table 6. *Distances* (Å) *and angles* (°) *in the thiopyran ring*

The standard deviation of the least significant figure is given in parentheses.

C(9)—C(10)	1·364 (17)
C(10)-C(11)	1·417 (20)
C(11)-C(12)	1·369 (23)
C(12)-S(1)	1·759 (17)
S(1) —C(15)	1·827 (13)
C(15)-C(19)	1·509 (18)
C(9)—C(10)-C(11)	124·5 (1·2)
C(10)-C(11)-C(12)	121·3 (1·4)
C(11)-C(12)-S(1)	121·7 (1·2)
C(12)-S(1) —C(15)	100·4 (0·7)
S(1) —C(15)-C(9)	109·4 (0·8)
C(15)-C(9)—C(10)	122·8 (1·1)

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