# The Crystal and Molecular Structure of Tetramethylthiuram Monosulphide

By Marcello Colapietro, Aldo Domenicano and Alessandro Vaciago*

*Università di Roma*, 00100 *Roma, and Laboratorio di Strutturistica Chimica del C.N.R. 'Giordano Giacomello'*, 00016 *Monterotondo Stazione, Italy*

The structure of tetramethylthiuram monosulphide has been determined from 1232 independent non-zero reflexions measured on an automated single-crystal diffractometer. Crystals are monoclinic, space group $P2_1/c$, with $a = 10\cdot170$ (3), $b = 7\cdot464$ (2), $c = 14\cdot092$ (5) Å, $\beta = 110\cdot55$ (2)°, $Z = 4$. The structure has been solved by direct methods and refined by full-matrix least squares to a final $R$ of 0·040. The results of a previous analysis by Tashpulatov [*Uzbek. Khim. Zh.* (1960), pp. 35–40] are shown to be in error. The molecule consists of two approximately planar dimethyldithiocarbamato moieties sharing an S atom; the two planes make an angle of 78·6°. An S atom from one moiety has a close intramolecular contact (3·112 Å) with the $sp^2$-hybridized C of the other; this leads to large differences between corresponding bond angles in the two moieties. It also causes a slight pyramidalization of the $sp^2$-hybridized C atom. A comparison of structural data for a variety of molecules containing the dialkyldithiocarbamato group shows that the S–C–N angles increase regularly with the lengths of the opposite C–S bonds.

## Introduction

As part of a research programme designed to provide an insight into the factors governing bond angles in $sp^2$-hybridized systems, and also in continuation of previous structural studies on metal dithiocarbamates and related compounds (Colapietro, Vaciago, Bradley, Hursthouse & Rendall, 1972, and references therein), we have determined the structure of tetramethylthiuram monosulphide:
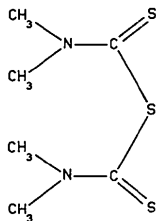


The results of a crystal structure analysis of this compound have been published (Tashpulatov, 1960). The analysis was carried out by two-dimensional techniques on two projections, and led to a final $R$ of 0·24 (the structure factor table is not given). We have used the published atomic and cell parameters to check the molecular geometry: the results obtained have cast doubt on the overall correctness of the structure. Apart from minor differences between the published bond distances and angles and those calculated by us, particularly alarming are the lengths of the intramolecular S···S contacts. The 'bites' of the two dithiocarbamato moieties in the molecule are 3·23 and 3·45 Å, respectively, to be compared with values of 3·03 Å in tetraethylthiuram disul-

phide (Karle, Estlin & Britts, 1967) and dicyclopenta-methylenethiuram disulphide (Dix & Rae, 1973), or 2·90 and 3·00 Å in dicyclopentamethylenethiuram monosulphide (Johnson & Paul, 1970).† Moreover, the distance between the terminal S atoms of the molecule is calculated to be only 2·73 Å, which is about 1 Å less than twice the van der Waals radius for S (Pauling, 1960, p. 260). We therefore decided to carry out an independent crystal structure analysis.

A preliminary account of this work was given at the Fifth Meeting of the Italian Crystallographic Association (Colapietro, Vaciago & Domenicano, 1971).

## Experimental

Bright yellow, prismatic crystals (m.p. 108–110°C) were grown by evaporation of an acetonic solution of the commercial product (Fluka). Photographs confirmed the crystals to be monoclinic, space group $P2_1/c$ ($C^5_{2h}$), as found by previous workers (Yamada & Mizuno, 1941; Tashpulatov, 1960). A crystal, *ca* 0·25 × 0·45 × 0·18 mm, was mounted on a Siemens AED automatic single-crystal diffractometer. Accurate values for the cell parameters were derived by a least-squares fit to the measured $\theta$ angles for 13 accurately centred reflexions. An independent measurement was made on a Syntex $P2_1$ diffractometer with 14 reflexions. The values from the two measurements are in excellent agreement, and compare reasonably well with those of Yamada & Mizuno (1941), whilst the agreement with Tashpulatov's (1960) results is poor (Table 1).

Intensities for the unique portion of the reciprocal lattice with $\sin\theta \le 0\cdot407$ were collected at room tem-

---

* To whom correspondence should be addressed at the Istituto di Fisica, Università di Roma, 00100 Roma, Italy.

† All values have been calculated from the atomic parameters quoted in the original papers.

perature on the Siemens diffractometer by the $\omega$-scan technique with Mo $K\alpha$ radiation filtered through 0·05 mm Zr foil. Two standard reflexions were monitored every 100 reflexions. Their intensities indicated no counter or crystal instability.

The intensities were corrected for Lorentz and polarization effects, but not for extinction or absorption ($\mu$ for Mo $K\alpha = 6·58$ cm$^{-1}$). 1547 independent structure amplitudes were derived, of which 1232 had $F_o > 3\sigma(F_o)$ and were used in all subsequent calculations.

## Structure determination and refinement

The structure was solved by a direct method (Karle & Karle, 1966). An $E$ map based on 130 reflexions with $|E| \geq 1·50$ showed three large peaks of comparable size which were interpreted as S atoms, plus a number of minor peaks among which the two N and six C atoms could be recognized.

A structure factor calculation based on the $E$ map gave an $R$ of 0·282. The positional and isotropic thermal parameters were refined by full-matrix least squares to an $R$ of 0·128. Allowance was then made for anisotropic thermal vibration, which reduced $R$ to 0·058. The function minimized was $\sum w(|F_o| - K|F_c|)^2$; the weighting scheme was based on the experimental $\sigma(F_o)$ derived from counting statistics.

At this stage a difference synthesis was computed from terms with $\sin \theta/\lambda \leq 0·40$. The 12 H atoms were seen as well-defined peaks. They were given isotropic temperature factors equal to those of the parent C

atoms at the end of the isotropic refinement. As a result $R$ fell to 0·046. Further full-matrix least-squares refinement of all the atomic parameters, with the H atoms treated isotropically, led to a final $R$ of 0·040 ($R_w = 0·054$). In the last cycle all the shifts were less than $\frac{1}{5}$ of the corresponding estimated standard deviations.

The scattering factors of Cromer & Mann (1968) were used for S, N and C. For H the values used were those of Hanson, Herman, Lea & Skillman (1964).

All calculations were carried out on the Univac 1108 computer of the University of Rome with local crystallographic programs (Domenicano, 1968; Domenicano, Spagna & Vaciago, 1969; Carruthers & Spagna, 1975).

## Results and discussion

Tables 2 and 3 give the final parameters for the atoms.* The molecular structure is shown in Fig. 1. Bond lengths and angles are reported in Table 4; they have been calculated with the cell parameters measured on the Siemens diffractometer.

A comparison of the present results with those of Tashpulatov (1960) shows the structure proposed by this author to be in error.

The molecule consists of two dimethyldithiocarbamato moieties sharing S(0), the other atoms being

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31799 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

---

## Table 1. Crystal data

Tetramethylthiuram monosulphide [bis(dimethylthiocarbamoyl) sulphide], $C_6H_{12}N_2S_3$, F.W. 208·38. Monoclinic, space group $P2_1/c$, $Z = 4$. $D_c = 1·38$, $D_m = 1·38$ g cm$^{-3}$ (by flotation in a mixture of carbon tetrachloride and $n$-hexane).

Unit-cell parameters (standard deviations are given in parentheses as units in the last digit)

|  | This work (Siemens diffractometer) | This work (Syntex diffractometer) | Yamada & Mizuno (1941) | Tashpulatov (1960) |
|---|---|---|---|---|
| $a$ (Å) | 10·170 (3) | 10·180 (3) | 10·22 | 9·72 |
| $b$ (Å) | 7·464 (2) | 7·468 (3) | 7·47 | 7·53 |
| $c$ (Å) | 14·092 (5) | 14·101 (5) | 13·99 | 13·60 |
| $\beta$ (°) | 110·55 (2) | 110·57 (3) | 110·45 | 110·13 |
| $V$ (Å$^3$) | 1001·6 (6) | 1003·7 (6) | 1001 | 934·6 |

## Table 2. Final coordinates ($\times 10^5$) and anisotropic thermal parameters ($\times 10^4$) for non-hydrogen atoms

Estimated standard deviations are given in parentheses as units in the last digit. The form of the anisotropic temperature factor is

$$T = \exp[-(h^2b_{11} + hkb_{12} + hlb_{13} + k^2b_{22} + klb_{23} + l^2b_{33})].$$

|  | $x$ | $y$ | $z$ | $b_{11}$ | $b_{12}$ | $b_{13}$ | $b_{22}$ | $b_{23}$ | $b_{33}$ |
|---|---|---|---|---|---|---|---|---|---|
| S(0) | 60649 (8) | 10530 (13) | 12551 (6) | 85 (1) | 11 (2) | 48·7 (5) | 259 (2) | −15 (1) | 49 (2) |
| S(1) | 81015 (9) | 11285 (14) | 34105 (7) | 92 (1) | 43 (3) | 32·9 (6) | 293 (2) | −18 (1) | 53 (3) |
| S(2) | 79753 (11) | −15656 (14) | 8724 (9) | 142 (1) | −8 (2) | 133·3 (9) | 169 (2) | −31 (2) | 105 (3) |
| N(1) | 53287 (27) | 12870 (35) | 28429 (20) | 95 (3) | 26 (6) | 73 (2) | 190 (5) | 7 (4) | 57 (7) |
| N(2) | 86064 (27) | 18911 (37) | 11974 (19) | 97 (3) | −17 (6) | 68 (2) | 159 (5) | −15 (4) | 56 (7) |
| C(1) | 64697 (33) | 11684 (41) | 25945 (23) | 94 (4) | 10 (7) | 62 (2) | 132 (6) | −7 (5) | 54 (8) |
| C(2) | 77430 (32) | 5405 (47) | 11468 (21) | 90 (4) | 18 (8) | 59 (2) | 200 (6) | 11 (4) | 42 (9) |
| C(11) | 54718 (54) | 13157 (79) | 39195 (33) | 155 (6) | 59 (13) | 123 (3) | 283 (10) | −4 (7) | 68 (16) |
| C(12) | 38927 (39) | 13048 (67) | 20987 (34) | 86 (4) | 18 (11) | 82 (3) | 249 (9) | −10 (6) | 79 (11) |
| C(21) | 99516 (43) | 15638 (69) | 10681 (39) | 115 (5) | −27 (11) | 114 (3) | 239 (10) | −12 (7) | 87 (12) |
| C(22) | 83791 (54) | 37414 (59) | 14010 (44) | 134 (6) | −33 (9) | 89 (4) | 181 (10) | −37 (8) | 94 (11) |

labelled S(1), C(1), *etc.* in one moiety and S(2), C(2), *etc.* in the other. In the present discussion the two halves of the molecule will be referred to as the 'first'

and 'second' moiety respectively. The conformation of the molecule is similar to that of the only other thiuram monosulphide whose structure has been determined by crystal structure analysis, dicyclopentamethylenethiuram monosulphide (Johnson & Paul, 1970), and even more so to that of several aryl sulphides (Table 5). Apart from the H atoms of the methyl groups each of the two dimethyldithiocarbamato moieties is
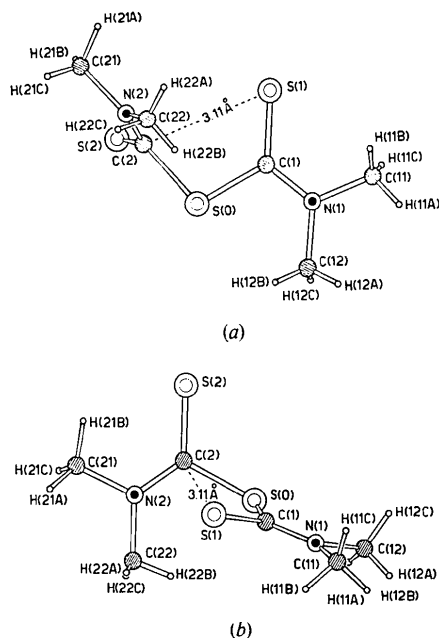


Fig. 1. Projections of the molecular structure of tetramethylthiuram monosulphide onto the least-squares planes through (a) the first and (b) the second dimethyldithiocarbamato moieties.
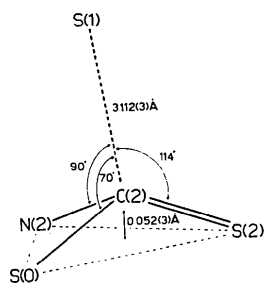


Fig. 2. Pyramidalization of C(2) in tetramethylthiuram monosulphide.

Table 3. *Final coordinates ($\times 10^3$) and isotropic thermal parameters for hydrogen atoms*

|        | $x$       | $y$       | $z$     | $B$ (Å$^2$)  |
|--------|-----------|-----------|---------|--------------|
| H(11A) | 469 (5)   | 194 (6)   | 399 (3) | 4·8 (1·1)    |
| H(11B) | 615 (6)   | 233 (8)   | 416 (4) | 6·1 (1·4)    |
| H(11C) | 563 (5)   | 30 (7)    | 418 (4) | 4·2 (1·3)    |
| H(12A) | 335 (5)   | 183 (6)   | 235 (3) | 3·0 (1·0)    |
| H(12B) | 383 (6)   | 205 (8)   | 151 (4) | 6·5 (1·4)    |
| H(12C) | 355 (5)   | 11 (8)    | 204 (4) | 5·6 (1·3)    |
| H(21A) | 1074 (8)  | 226 (11)  | 168 (6) | 11·2 (2·1)   |
| H(21B) | 1009 (5)  | 24 (9)    | 109 (4) | 6·7 (1·5)    |
| H(21C) | 995 (6)   | 204 (7)   | 52 (4)  | 5·8 (1·4)    |
| H(22A) | 900 (5)   | 409 (6)   | 194 (4) | 4·1 (1·2)    |
| H(22B) | 751 (7)   | 388 (7)   | 148 (4) | 6·8 (1·6)    |
| H(22C) | 836 (5)   | 446 (7)   | 88 (3)  | 4·4 (1·2)    |

Table 4. *Bond lengths and angles in tetramethylthiuram monosulphide*

Standard deviations are given in parentheses as units in the last digit.

(a) Bond lengths (Å)

| C(1)–S(0)  | 1·787 (3) | C(2)–S(0)   | 1·807 (4) |
|------------|-----------|-------------|-----------|
| C(1)–S(1)  | 1·655 (3) | C(2)–S(2)   | 1·655 (4) |
| C(1)–N(1)  | 1·327 (5) | C(2)–N(2)   | 1·322 (4) |
| N(1)–C(11) | 1·473 (6) | N(2)–C(21)  | 1·463 (6) |
| N(1)–C(12) | 1·469 (4) | N(2)–C(22)  | 1·446 (5) |

The C–H bond lengths range between 0·83 (5) and 1·08 (7) Å, mean 0·93 (2) Å.

(b) Bond angles (°)

| S(0)—C(1)–S(1)     | 122·4 (2) | S(0)—C(2)–S(2)    | 115·9 (2) |
|--------------------|-----------|-------------------|-----------|
| S(0)—C(1)–N(1)     | 112·5 (2) | S(0)—C(2)–N(2)    | 117·6 (3) |
| S(1)—C(1)–N(1)     | 125·1 (3) | S(2)—C(2)–N(2)    | 126·2 (3) |
| C(1)—N(1)–C(11)    | 119·6 (3) | C(2)—N(2)–C(21)   | 119·9 (3) |
| C(1)—N(1)–C(12)    | 123·7 (3) | C(2)—N(2)–C(22)   | 126·1 (4) |
| C(11)–N(1)–C(12)   | 116·7 (4) | C(21)–N(2)–C(22)  | 114·0 (4) |

C(1)–S(0)–C(2)   103·0 (1)

Table 5. *Geometry of the C(1)–S(0)–C(2) region and molecular conformation in some thiuram and aryl monosulphides*

Bond lengths are in Å, angles in degrees. Estimated standard deviations (when given) are in parentheses as units in the last digit.

|                                                         | Reference | C(1)–S(0) | C(2)–S(0) | C(1)–S(0)–C(2) | $\tau_1{}^a$ | $\tau_2{}^b$ | $\tau_{12}{}^c$ |
|---------------------------------------------------------|-----------|-----------|-----------|----------------|--------------|--------------|------------------|
| Dicyclopentamethylenethiuram monosulphide               | d         | 1·795 (5) | 1·805 (5) | 103·3 (3)      | 23·0$^e$     | 61·9$^e$     | 70·5$^e$         |
| Tetramethylthiuram monosulphide                         | f         | 1·787 (3) | 1·807 (4) | 103·0 (1)      | 9·3          | 80·2         | 78·6             |
| p-Dimethylaminophenyl phenyl sulphide                   | g         | 1·769 (4) | 1·786 (4) | 104·1 (2)      | 4·5          | 84·8         | 82·2             |
| 2-(4'-Carbomethoxy-2'-nitrothio-phenyl)-1,3,5-trimethylbenzene | h  | 1·759 (2) | 1·785 (3) | 102·9 (1)      | 4·2          | 86·8         | 88·4             |
| trans-3-p-Tolylthiocinnamic acid                        | i         | 1·738 (6) | 1·764 (7) | 104·4 (3)      | 5·0$^e$      | 64·9$^e$     | 67·3$^e$         |

(a) Angle between the C(1)–S(0)–C(2) plane and the least-squares plane of the molecular fragment at C(1). (b) Angle between the C(1)–S(0)–C(2) plane and the least-squares plane of the molecular fragment at C(2). (c) Angle between the two least-squares planes. (d) Johnson & Paul (1970). (e) Calculated from the atomic parameters quoted in the original paper. (f) This work. (g) Bandoli, Clemente, Tondello & Dondoni (1974). (h) van der Heijden, Chandler & Robertson (1975). (i) Stephens (1970).

approximately (but not perfectly, see Table 6) planar; the angle between the two least-squares planes, $\tau_{12}$, is 78·6°. The two halves of the molecule are oriented in quite different ways with respect to the C(1)–S(0)–C(2) plane, the dihedral angles being $\tau_1 = 9\cdot3$ and $\tau_2 = 80\cdot2°$ respectively. The value of the C(1)–S(0)–C(2) bond angle, 103·0 (1)°, is in close agreement with the other values reported in Table 5.

All bond lengths in the molecule compare well with the corresponding lengths in other thiuram mono and disulphides. (A detailed comparison of the bond lengths and angles at the $sp^2$-hybridized C atoms in thiuram sulphides as well as in metal complexes of unidentate dialkyldithiocarbamato ligands is given in

### Table 6. Least-squares planes

(a) Plane through the first dimethyldithiocarbamato moiety. Equation of the plane (referred to the crystallographic axes):

$$-0\cdot5122x - 7\cdot4512y + 0\cdot6409z = -1\cdot0307.$$

Displacements (Å) of atoms from the plane (standard deviations in the atomic positions are given in parentheses as units in the last digit)

| | | | |
|---|---|---|---|
| S(0) | −0·016 (1) | N(1) | 0·019 (3) |
| S(1) | 0·007 (1) | C(11) | −0·021 (5) |
| C(1) | 0·005 (3) | C(12) | 0·006 (5) |

(b) Plane through the second dimethyldithiocarbamato moiety. Equation of the plane

$$0\cdot7906x - 1\cdot2923y + 12\cdot5712z = 1\cdot9406.$$

Displacements (Å) of atoms from the plane:

| | | | |
|---|---|---|---|
| S(0) | 0·019 (1) | N(2) | −0·001 (3) |
| S(2) | 0·011 (1) | C(21) | 0·013 (5) |
| C(2) | −0·043 (3) | C(22) | 0·000 (5) |

Table 7.) The lengths of the C–N and terminal C–S bonds are intermediate between the values expected for single and double bonds, thus indicating that the canonical form (II) makes a substantial contribution



to the structure. This is in accordance with the results of $^1$H NMR studies of the thiuram mono and disulphides in solution, which give evidence for hindered rotation about the central C–N bonds (Brinkhoff, Grotens & Steggerda, 1970; Wilson, 1971). The high double-bond character of these bonds also affects the C–N stretching frequencies of the infrared spectrum, which are shifted considerably towards higher frequency from the normal C–N region (Wilson, 1971).

An important feature in the solid-state molecular structure of tetramethylthiuram monosulphide is the marked difference in the pattern of intramolecular non-bonded interactions between the two dimethyldithio-carbamato moieties (Fig. 1). Whilst S(2) is far away from the first moiety, S(1) approaches close to the second, pointing towards C(2). The length of the S(1)···C(2) contact is indeed only 3·112 (3) Å; also short is the length of the S(1)···N(2) contact, 3·382 (3) Å. Values of 3·5–3·6 Å could have been predicted from the sum of the van der Waals radius of S and the half-thickness of an aromatic molecule (Pauling, 1960, p. 260).
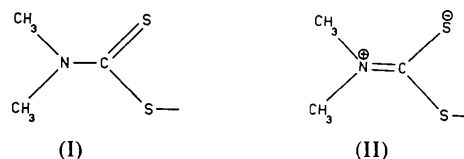
Table 7. *Bond lengths and angles at the $sp^2$-hybridized carbons in compounds containing dialkyldithiocarbamato groups*

Bond lengths are in Å, angles in degrees. Estimated standard deviations, $\sigma$, are given in parentheses as units in the last digit. Only compounds with $\sigma(\text{S–C–S}') \le 0\cdot7°$ have been considered for inclusion in this table.

| | Reference | C–S | S'–C–N | C–S' | S–C–N | C–N | S–C–S' |
|---|---|---|---|---|---|---|---|
| Tetramethylthiuram monosulphide | a | 1·655 (3) | 112·5 (2) | 1·787 (3) | 125·1 (3) | 1·327 (5) | 122·4 (2) |
| | | 1·655 (4) | 117·6 (3) | 1·807 (4) | 126·2 (3) | 1·322 (4) | 115·9 (2) |
| Dicyclopentamethylenethiuram monosulphide | b, c | 1·636 (6) | 113·3 (4) | 1·795 (6) | 124·9 (4) | 1·344 (8) | 121·8 (3) |
| | | 1·656 (6) | 118·6 (4) | 1·805 (6) | 127·6 (4) | 1·289 (7) | 113·6 (3) |
| Tetramethylthiuram disulphide | d | 1·634 (13) | 111·3 (9) | 1·829 (15) | 126·6 (9) | 1·319 (15) | 122·1 (6) |
| Tetraethylthiuram disulphide | e, c | 1·662 (11) | 113·4 (8) | 1·813 (14) | 124·6 (9) | 1·334 (15) | 122·0 (7) |
| | | 1·634 (11) | 112·1 (8) | 1·818 (12) | 125·6 (9) | 1·362 (14) | 122·2 (7) |
| Dicyclopentamethylenethiuram disulphide | f | 1·649 (3) | 111·3 (2) | 1·810 (3) | 126·8 (2) | 1·329 (3) | 121·9 (1) |
| | | 1·647 (3) | 110·9 (2) | 1·819 (3) | 127·2 (2) | 1·330 (3) | 121·9 (1) |
| S-t-Butyl-N,N-dimethyltrithioperoxy-carbamate | g, c | 1·651 (13) | 110·5 (9) | 1·804 (11) | 125·8 (8) | 1·351 (14) | 123·6 (6) |
| Sodium diethyldithiocarbamate trihydrate | h | 1·712 (7) | 120·1 (5) | 1·729 (6) | 119·5 (5) | 1·344 (8) | 120·4 (4) |
| Arsenic(III) diethyldithiocarbamate | i | 1·678 (10) | 117·5 (7) | 1·752 (8) | 123·0 (6) | 1·345 (12) | 119·5 (5) |
| | | 1·694 (9) | 118·1 (7) | 1·767 (9) | 123·6 (7) | 1·331 (10) | 118·2 (4) |
| | | 1·655 (11) | 116·7 (8) | 1·764 (10) | 123·2 (7) | 1·341 (14) | 120·2 (6) |

(a) This work. (b) Johnson & Paul (1970). (c) The standard deviations given here have been calculated from the standard deviations on the atomic parameters quoted in the paper. (d) Marøy (1965, 1971). (e) Karle, Estlin & Britts (1967). (f) Dix & Rae (1973). (g) Mitchell (1969). Bond distances and angles have been calculated from the atomic parameters quoted in the paper. (h) Colapietro, Domenicano & Vaciago (1968). (i) Colapietro, Domenicano, Scaramuzza & Vaciago (1968), and unpublished results.

The close approach of S(1) to the second moiety gives rise to highly significant discrepancies between corresponding bond angles in the two halves of the molecule (Table 4). The overall effect may best be described as a systematic increase of the various bond angles along the S(1)–C(1)–S(0)–C(2)–N(2)–C(22) chain, so as to provide more room for the approaching S(1) atom.*

A similar pattern of intramolecular non-bonded interactions may be recognized in dicyclopentamethyl-enethiuram monosulphide (Johnson & Paul, 1970), as a consequence of the similar conformation of the two molecules. From the published atomic parameters, the S(1)···C(2) and S(1)···N(2) contact distances are calculated to be 3·152 (6) and 3·353 (4) Å respectively. Inspection of the reported molecular geometry (Table 7) shows a pattern of differences between corresponding bond angles at the $sp^2$-hybridized C atoms very close to that observed here.

On the other hand, no difference greater than $3\sigma$ between corresponding bond angles at the $sp^2$-hybridized atoms is observed in tetraethylthiuram disulphide (Karle, Estlin & Britts, 1967) and dicyclopentamethyl-enethiuram disulphide (Dix & Rae, 1973). It may be added that in tetramethylthiuram disulphide (Marøy, 1965) the two halves of the molecule are required to be equivalent by space-group symmetry. In these molecules the terminal S atom of each dithiocarbamato moiety is 3·8–3·9 Å from the central, $sp^2$-hybridized C of the other moiety. Strong intramolecular non-bonded interactions and structural non-equivalence of the two halves of the molecule seem to be peculiar to the thiuram monosulphides.

The large differences between chemically equivalent bond angles in tetramethylthiuram monosulphide are not paralleled by correspondingly large differences in the lengths of chemically equivalent bonds. The two C–S 'double' bonds happen to have exactly equal length, 1·655 (3) and 1·655 (4) Å, and the lengths of the two central C–N bonds are equal within experimental error [1·327 (5) and 1·322 (4) Å]. Also the lengths of the four N–CH$_3$ bonds are in reasonable agreement.†

There is one important exception, however. The lengths of the two C–S 'single' bonds, 1·787 (3) and 1·807 (4) Å, differ by about $6\sigma$. Comparable differences are also observed in the other compounds of Table 5. In all cases the shorter C–S bond is that associated with the smaller dihedral angle, $\tau_1$, i.e. with that molecular fragment which is almost coplanar with the C(1)–S(0)–C(2) system.

This systematic effect, which has recently been ob-

---

* The angle at S(0) is unique and cannot, of course, be considered as increased.

† The situation is, therefore, somewhat different from that in dicyclopentamethylenethiuram monosulphide (Johnson & Paul, 1970), where some of the discrepancies between chemically equivalent bond lengths appear to be significant (Table 7).

served in several diaryl ethers and sulphides (van der Heijden, Chandler & Robertson, 1975), indicates an appreciable interaction between the filled $3p_z$ orbital of S(0) and the $\pi$ system of the favourably oriented molecular fragment. It should be noted that the orientation of the other fragment with respect to the C(1)–S(0)–C(2) plane is such as to favour a (presumably much weaker) interaction of its $\pi$ system with the empty $3d_{xy}$ orbital of S(0) (Domenicano, Vaciago & Coulson, 1975).

An interesting effect of the short S(1)···C(2) contact in tetramethylthiuram monosulphide is a slight pyramidalization of the thiocarbonyl C(2), as shown in Fig. 2. The 0·052 (3) Å displacement of C(2) from the S(0), S(2), N(2) plane towards S(1) is indicative of the attractive character of the S(1)···C(2) interaction, and is in keeping with the observations of Bürgi, Dunitz & Shefter (1973, 1974) on the effect of the N···C=O and O···C=O interactions on the coordination geometry of the carbonyl C atom. The corresponding displacement in dicyclopentamethylenethiuram monosulphide (Johnson & Paul, 1970), as calculated from the published atomic coordinates, is 0·041 (5) Å. The displacement of the other thiocarbonyl C(1), from its coordination plane, is less than 0·001 Å in both molecules.

It is well known that among the several factors affecting the values of bond angles in $sp^2$ (and $sp^3$) hybridized centres an important role is played by the repulsions between bonding (and non-bonding) electron pairs in the valence shell of the central atom (Gillespie, 1972, and references therein). In a recent survey of the molecular geometries of urea derivatives (Domenicano, Vaciago & Coulson, 1974) the value of the N–C–N angle has been found to increase regularly with the length of the opposite bond, C–O. This result is easily accounted for in terms of varying repulsions between bonding electron pairs in the valence shell of C. [Marked deviations have been found to occur in two classes of compounds, namely (i) overcrowded N-substituted ureas and (ii) cyclic urea derivatives. It is clear that, in addition to the electron pair repulsions, other factors are important in these systems.]

We wondered if correlations of a similar type occurred with molecules containing the dithiocarbamato moiety, and have looked at the effect that variations in the lengths of the C–S and C–N bonds have on the opposite angles at C. Table 7 shows relevant details of the molecular geometry in a number of compounds containing dialkyldithiocarbamato groups. (Chelated metal complexes of the dialkyldithiocarbamato ligands have not been included, since chelation may be expected to affect the bond angles at C.) If the values of the S–C–N angles from Table 7 are plotted against the lengths of the opposite C–S bonds a good correlation is obtained (Fig. 3a). The trend of the correlation line is closely reminiscent of that observed in the plot of N–C–N $vs$ $d_{C-O}$ in urea derivatives (Domenicano, Vaciago & Coulson, 1974). As in that case, the correlation becomes linear if the C–S bond number (Pauling,

1960, p. 236) or VB bond order is used as the abscissa instead of the bond length (Fig. 3b).
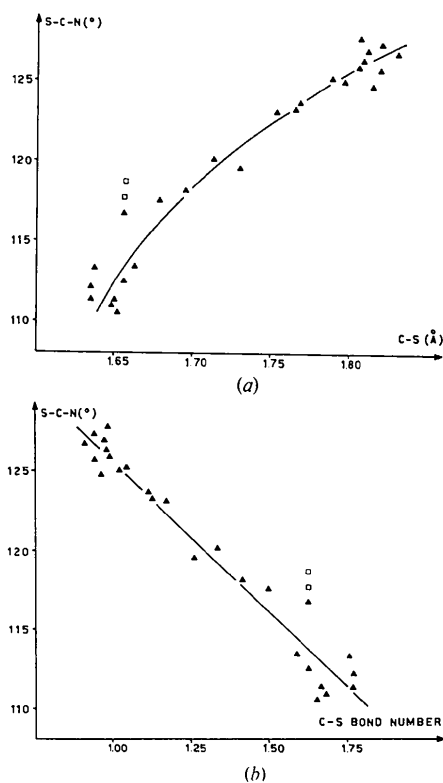


*(a)*



*(b)*

Fig. 3. Plots of the S–C–N angle vs (a) the length, $d_{C-S}$, and (b) the bond number, $n_{C-S}$, (Pauling, 1960, p. 236) of the opposite C–S bond for compounds containing dialkyldithiocarbamato groups. The data used are taken from Table 7. The equation of the least-squares line in (b) is S–C–N = $-18.93n_{C-S} + 144.5$, with a correlation coefficient of 0.98 on 26 data sets. The two points shown as open squares have not been included in the calculation of the least-squares line; they are associated with the S(0)–C(2)–N(2) angles of tetramethylthiuram and dicyclopentamethylenethiuram monosulphides (see text). C–S bond numbers have been calculated from C–S bond lengths assuming a parabolic relationship, $d_{C-S} = an^2_{C-S} + bn_{C-S} + c$, and imposing $n_{C-S}$ to be 1.00, 1.33₃, and 2.00 when $d_{C-S}$ is 1.80, 1.71₂, and 1.61 Å respectively. This gives $a = 0.111$, $b = -0.523$, and $c = 2.212$. [The first and third points used to define the parabola correspond to sound estimates of the lengths of the C($sp^2$)–S single and double bonds, respectively, based on a variety of literature data (Abrahams, 1956; Lide, 1962; Sutton, 1965; Baenziger & Duax, 1968). The second point is based on the geometry of the trithiocarbonate anion, as obtained from a crystal structure analysis of potassium trithiocarbonate monohydrate (Philippot & Lindqvist, 1970).]

The two experimental points showing the largest (positive) deviation from the correlation line are associated with the S(0)–C(2)–N(2) angles of tetramethylthiuram and dicyclopentamethylenethiuram monosulphides; they are shown as open squares in Fig. 3. As pointed out above, the close approach of S(1) to C(2) in these molecules gives rise to a marked increase

of some bond angles, including S(0)–C(2)–N(2). From the deviations of the two points relative to the correlation line, the S(0)–C(2)–N(2) angle is estimated to be 4–5° greater than expected on the basis of purely electronic effects.

Unlike the S–C–N angles, the angle S–C–S is not correlated with the length of the opposite bond, C–N. This may partly be due to the more limited range of values available for the lengths of the C–N bonds in Table 7, compared with the C–S bonds. It may also indicate, however, an inherently lower sensitivity of the S–C–S angle to changes in the repulsions between bonding electron pairs in the valence shell of C.

## References

ABRAHAMS, S. C. (1956). *Quart. Rev.* **10**, 407–436.
BAENZIGER, N. C. & DUAX, W. L. (1968). *J. Chem. Phys.* **48**, 2974–2981.
BANDOLI, G., CLEMENTE, D. A., TONDELLO, E. & DONDONI, A. (1974). *J. Chem. Soc. Perkin* II, pp. 157–160.
BRINKHOFF, H. C., GROTENS, A. M. & STEGGERDA, J. J. (1970). *Rec. Trav. Chim. Pays-Bas*, **89**, 11–17.
BÜRGI, H. B., DUNITZ, J. D. & SHEFTER, E. (1973). *J. Amer. Chem. Soc.* **95**, 5065–5067.
BÜRGI, H. B., DUNITZ, J. D. & SHEFTER, E. (1974). *Acta Cryst.* B**30**, 1517–1527.
CARRUTHERS, J. R. & SPAGNA, R. (1975). Ital. Crystallogr. Assoc., 7th Meet., Bologna, Italy. Abstracts, pp. 65–67.
COLAPIETRO, M., DOMENICANO, A., SCARAMUZZA, L. & VACIAGO, A. (1968). *Chem. Commun.* pp. 302–303.
COLAPIETRO, M., DOMENICANO, A. & VACIAGO, A. (1968). *Chem. Commun.* pp. 572–573.
COLAPIETRO, M., VACIAGO, A., BRADLEY, D. C., HURSTHOUSE, M. B. & RENDALL, I. F. (1972). *J. Chem. Soc. Dalton*, pp. 1052–1057.
COLAPIETRO, M., VACIAGO, A. & DOMENICANO, A. (1971). Ital. Crystallogr. Assoc., 5th Meet., Bari, Italy. Abstracts, pp. 13–14.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
DIX, M. F. & RAE, A. D. (1973). *Cryst. Struct. Commun.* **2**, 159–162.
DOMENICANO, A. (1968). Ital. Crystallogr. Assoc., 2nd Meet., Parma, Italy. Abstracts, pp. 47–48.
DOMENICANO, A., SPAGNA, R. & VACIAGO, A. (1969). *Atti Accad. Naz. Lincei, Rend. Classe Sci. Fis. Mat. Nat.* **47**, 331–336.
DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1974). Second Eur. Crystallogr. Meet., Keszthely, Hungary. Abstracts, pp. 436–438.
DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* B**31**, 1630–1641.
GILLESPIE, R. J. (1972). *Molecular Geometry.* London: Van Nostrand-Reinhold.
HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
HEIJDEN, S. P. N. VAN DER, CHANDLER, W. D. & ROBERTSON, B. E. (1975). *Canad. J. Chem.* **53**, 2102–2107.

JOHNSON, P. L. & PAUL, I. C. (1970). *J. Chem. Soc. (B)*, pp. 1296–1303.

KARLE, I. L., ESTLIN, J. A. & BRITTS, K. (1967). *Acta Cryst.* **22**, 273–280.

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.

LIDE, D. R. (1962). *Tetrahedron*, **17**, 125–134.

MARØY, K. (1965). *Acta Chem. Scand.* **19**, 1509.

MARØY, K. (1971). Personal communication.

MITCHELL, D. J. (1969). *Acta Cryst.* **B25**, 998–1001.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

PHILIPPOT, E. & LINDQVIST, O. (1970). *Acta Cryst.* **B26**, 877–881.

STEPHENS, F. S. (1970). *J. Chem. Soc. (A)*, pp. 1843–1846.

SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Supplement. London: The Chemical Society.

TASHPULATOV, YU. (1960). *Uzbek. Khim. Zh.* pp. 35–40.

WILSON, N. K. (1971). *J. Phys. Chem.* **75**, 1067–1072.

YAMADA, T. & MIZUNO, K. (1941). *J. Soc. Chem. Ind. Japan*, **44**, 708–709.

# 9-Methyl-9β,10α-oestr-4-en-3-one-17β-ol p-Bromobenzoate

BY G. J. KRUGER AND J. COETZER

*National Physical Research Laboratory, CSIR, P.O. Box 395, Pretoria 0001, South Africa*

$C_{26}H_{25}O_3Br$, monoclinic, space group $P2_1$; $a = 16·84$ (2), $b = 13·26$ (1), $c = 10·18$ (1) Å, $\beta = 95·43$ (5)°; $Z = 4$, $M = 465·39$, $D_x = 1·37$, $D_m = 1·36$ g cm$^{-3}$. The conformation of the unsaturated 4-en-3-one $A$ ring is midway between a sofa and a half-chair. The conformations of the two unrelated molecules in the asymmetric unit do not differ significantly.

## Introduction

The total synthesis of 17β-hydroxy-9-methyl-9β,10α-oestr-4-en-3-one (Bull & Tuinman, 1972, 1973) is part of a study of the properties of skeletally modified steroids through the synthesis of steroids possessing the 9-methyl-19-nor-9β,10α-skeleton (Bull, Floor & Tuinman, 1975). The structure determination of the title compound was undertaken in order to confirm the structure assigned to this steroid.

The lattice parameters and intensities were measured on a Philips PW 1100 four-circle diffractometer in the

$\omega$–$2\theta$ mode with graphite-monochromated Mo $K\alpha$ radiation and a crystal $0·2 \times 0·2 \times 0·2$ mm. The systematic absences $k = 2n + 1$ for 0$k$0 indicated space group $P2_1$. Data were collected at a scan rate of $0·02°$ s$^{-1}$ and a constant scan width of $0·8°$ in the range $\theta = 3$ to 22°. The background was counted for half the total scanning time on each side of a reflexion. 2915 independent reflexions were measured of which 711 were considered unobserved with $I < 1·65\sigma$. No absorption corrections were applied ($\mu = 19·5$ cm$^{-1}$).

The structure was solved by conventional Patterson and Fourier techniques; H atoms, except those of the methyl groups, were located from a difference synthesis. Refinement was by least squares. In the final cycles non-hydrogen atoms were given anisotropic temperature factors and H atoms a constant isotropic temperature factor equal to the overall value estimated from a Wilson plot. The function minimized was $\sum w(\Delta F)^2$ with $1/\sigma_F^2$ weights. $R = \sum \Delta F / \sum F_o$ and $R_w = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2}$ converged to 0·055 and 0·061 respectively.

All calculations were done with the X-RAY system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The scattering factors of Stewart, Davidson & Simpson (1965) were used for H; those for all other atoms were generated from the analytical expressions of Cromer & Mann (1968). Final atomic parameters are given in Tables 1 and 2.*
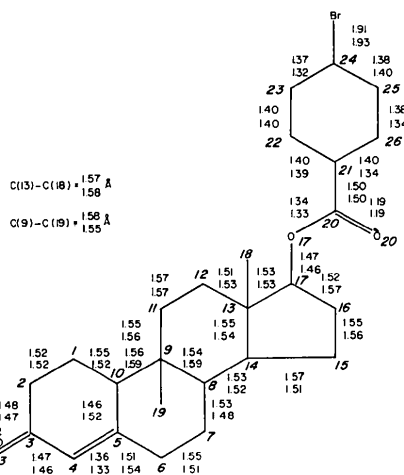
Fig. 1. Nomenclature and interatomic distances. Values for molecules $A$ and $B$ are given above and below respectively.