The crystal and molecular structure of t-butyl *N,N*-dimethyltrithiopercarbamate, $C_7H_{15}NS_3$. By DONALD J. MITCHELL,* *U. S. Naval Research Laboratory, Washington, D. C.* 203 90, *U.S.A.*

Tertiary butyl *N,N*-dimethyltrithiopercarbamate $(CH_3)CSSCN(CH_3)_2$ crystallizes in space group $P2_1/c$ with cell parameters $a=6\cdot21\pm0\cdot02$, $b=17\cdot35\pm0\cdot03$, $c=10\cdot66\pm0\cdot02$ Å, $\beta=104°07'$ and $Z=4$. The structure was solved by direct methods. The $C{-}N{<}^C_C$ group was found to be planar with a C–N bond length of $1\cdot35$ Å for the bond adjacent to the sulfur atoms. The –C–S–S–C– group has the peroxide configuration with a dihedral angle of $99\cdot6°$. The C=S and S–S distances were found to be $1\cdot65$ and $2\cdot00$ Å, respectively.

Tertiary butyl *N,N*-dimethyltrithiopercarbamate, first synthesized by Schulye, Short & Crouch (1950) and in an alternate manner by Buckman (1965) has been found to be an effective insect repellent (Goodhue & Tissol, 1952; Goodhue, 1960), seed disinfectant (Goodhue & Florence, 1952) and vulcanization accelerator (Svetlich, 1958). The material crystallizes in space group $P2_1/c$ with four molecules to the unit cell. Cell parameters are $a=6\cdot21\pm0\cdot02$, $b=17\cdot35\pm0\cdot03$ and $c=10\cdot66\pm0\cdot02$ Å and $\beta=104°07'\pm10'$.

The crystal was mounted on the *a* axis and the zero through the fourth layers were recorded by the use of multiple film, equi-inclination Weissenberg techniques with Cu radiation and a Ni filter. The X-ray intensities were estimated by visual comparison with a calibrated film strip. After corrections were made for the Lorentz and polarization factors and spot size, normalized structure factors were computed. A total of 1498 reflections were recorded.

Phases were determined directly from the intensities by means of the symbolic addition procedure (Karle & Karle, 1963, 1966). To begin the phase determination the origin was specified by assigning + signs to the independent reflections 217, 347, and 171, which had $|E|$ values of $4\cdot42$, $4\cdot16$ and $3\cdot00$ respectively. On the basis of these assignments alone, phases for 416 reflections were determined by the Σ_2 relationship. There was no need to assign unknown symbols to any reflections. An E map computed with these data gave the positions of all the atoms.

The positions of the atoms were refined by a least-squares minimization of the function $\Sigma (F_o - F_c)^2$ (Busing, Martin & Levy, 1962) with first isotropic and then anisotropic temperature factors. The scale factors for the individual layers were not varied during the anisotropic refinement. Difficulties in the anisotropic refinement arose when the temperature factor for C(3) persisted in becoming negative. Finally it was kept constant at the value determined in the isotropic refinement. The final R value for all the observed data was $11\cdot6\%$ (Table 1). Coordinates are listed in Table 2. The conformation of the molecule and the bond distances are shown in Fig. 1, which was prepared with the use of the Oak Ridge *ORTEP* program (Johnson, 1965). The crystal was lost before its dimensions were measured and absorption corrections could not be made. Hence no physical meaning was attached to the size and shape of the

anisotropic temperature factors and they are represented as spheres in Fig. 1. Interatomic distances and angles are given in Table 3.

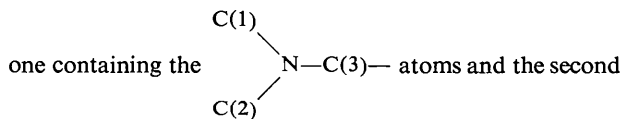The most striking feature of the molecule is the near planarity of the ${}^{C(1)\,}_{C(2)}{>}C{-}C(3){-}S(2){-}$ group with S(1) double-bonded to C(3).
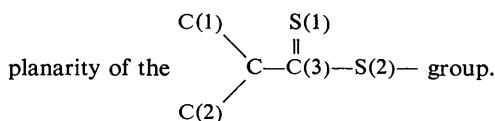
The least-squares equation for this group of atoms referred to the monoclinic axes is,

$$3\cdot3804x + 14\cdot3860y - 0\cdot09398z = 14\cdot1980, \qquad (1)$$

where the value on the right-hand side is the distance from the unit-cell origin to the plane. The deviations from this plane are:

	Deviation
C(1)	$+0\cdot06$ Å
C(2)	$-0\cdot02$
N	$-0\cdot05$
C(3)	$-0\cdot03$
S(1)	$-0\cdot01$
S(2)	$+0\cdot05$

These atoms may also be thought of as forming two planes, one containing the ${}^{C(1)\,}_{C(2)}{>}N{-}C(3){-}$ atoms and the second containing $-N{-}C(3){-}S(2)-$ with S(1) double-bonded to C(3), whose equations are:

$$3\cdot2610x + 14\cdot6717y - 0\cdot3658z = 14\cdot2289, \qquad (2)$$

$$3\cdot4390x + 14\cdot1685y - 0\cdot2452z = 14\cdot1772. \qquad (3)$$

The deviations from planarity for these atoms are:

Plane (2)		Plane (3)	
C(1)	$+0\cdot01$ Å	N	$-0\cdot01$ Å
C(2)	$+0\cdot01$	C(3)	$+0\cdot005$
N	$-0\cdot04$	S(1)	$+0\cdot004$
C(3)	$+0\cdot01$	S(2)	$+0\cdot003$

* Present address: Department of Chemistry, Juniata College, Huntingdon, Pa. 16652, U.S.A.

Table 1. *Observed and calculated structure factors*
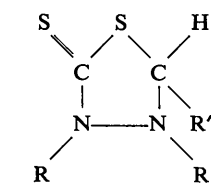The columns are *l*, |F_{obs}| and F_{calc}.

The angle between these two planes (the rotation about the N–C(3) bond) is 4·5 degrees. Similar planar arrangements of this kind of group have been found in:
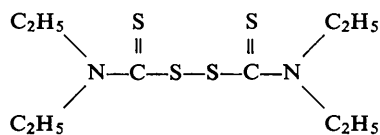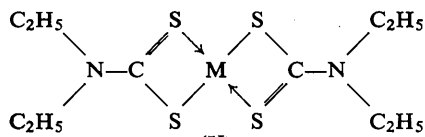
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C2H5         S          S         C2H5
   \         ||         ||        /
    N—C—S—S—C—N
   /                              \
C2H5                              C2H5
```
(I)
(Karle, Estlin & Britts, 1967)

```
C2H5     S      S       C2H5
   \     ∕      ∕ \      /
    N—C      M      C—N
   /     \  ∕ ↑     ∕     \
C2H5     S      S       C2H5
```
(II)
(Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965)

and

```
S    S      H
 \\ / \    /
   C    C
   |    | \
   N———N   R'
  /        \
 R          R
```
(III)
(Karle & Karle, 1964)
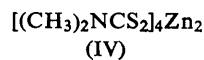
$$[(CH_3)_2NCS_2]_4Zn_2$$
(IV)
(Klug, 1966).

In each case, the C–N bond adjacent to the C=S has some double bond character. Its length falls in the range 1·32–1·36 Å as compared with 1·44–1·51 Å for the other carbon

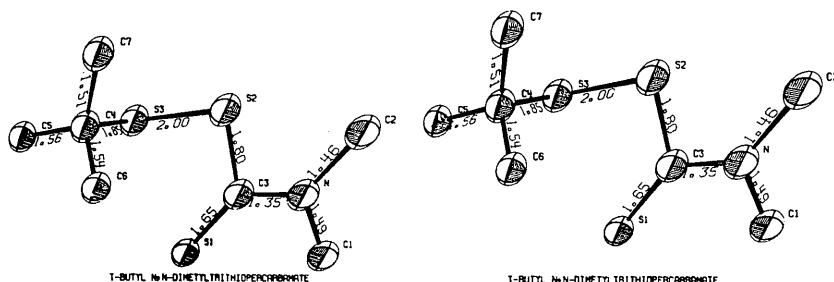Table 2. *Fractional coordinates of t-butyl N,N-dimethyltrithiopercarbamate*

	x	$\sigma_x \times 10^{4*}$	y	$\sigma_y \times 10^4$	z	$\sigma_z \times 10^4$
C(1)	0·5998	26	0·8548	7	0·7011	10
C(2)	0·2456	25	0·9321	8	0·6405	11
N	0·4173	17	0·8893	5	0·5981	8
C(3)	0·4361	20	0·8857	6	0·4746	9
S(1)	0·6327	6	0·8400	2	0·4243	3
S(2)	0·2194	6	0·9412	2	0·3697	3
S(3)	0·2695	6	0·9318	2	0·1916	3
C(4)	0·0713	22	0·8574	6	0·1091	10
C(5)	0·1316	35	0·8523	13	−0·0253	13
C(6)	0·1068	31	0·7826	7	0·1890	16
C(7)	−0·1644	26	0·8859	8	0·0902	13

* The σ's are those computed in the least-squares refinement.

Table 3. *Interatomic distances and angles for t-butyl N,N-dimethyltrithiopercarbamate*

C(1)–N	1·49 ± 0·02	C(2)–N——C(1)	117·3 °*
C(2)–N	1·46 ± 0·02	C(2)–N——C(3)	124·6
C(3)–N	1·35 ± 0·02	C(1)–N——C(3)	117·7
C(3)–S(1)	1·65 ± 0·02	N——C(3)–S(2)	110·4
C(3)–S(2)	1·80 ± 0·02	N——C(3)–S(1)	125·7
S(2)–S(3)	2·00 ± 0·01	C(3)–S(2)–S(3)	106·1
S(3)–C(4)	1·85 ± 0·02	S(2)–S(3)–C(4)	105·4
C(4)–C(5)	1·56 ± 0·03	S(3)–C(4)–C(5)	101·1
C(4)–C(6)	1·54 ± 0·03	S(3)–C(4)–C(6)	109·8
C(4)–C(7)	1·51 ± 0·03	S(3)–C(4)–C(7)	110·2
		C(5)–C(4)–C(6)	114·9
		C(5)–C(4)–C(7)	109·7
		C(6)–C(4)–C(7)	110·7

* The standard deviations for the bond angles are approximately 1·0°.

T-BUTYL N,N-DIMETHYLTRITHIOPERCARBAMATE   T-BUTYL N,N-DIMETHYLTRITHIOPERCARBAMATE

Fig. 1. Stereodiagram showing the conformation of t-butyl *N,N*-dimethyltrithiopercarbamate (Johnson, 1965).

nitrogen bonds in the above five molecules. The C = S bond in the present study is 1·65 Å as compared with 1·63–1·66 Å for molecules I and III, 1·70 Å for molecule II, 1·70 and 1·75 Å for molecule IV, and 1·71–1·72 Å for various thiourea derivatives (Truter, 1960; Dias & Truter, 1964; Wheatley, 1953).

The C–S–S–C group has the peroxide configuration with a dihedral angle of 99·6° as compared with 96·4° for I, 93° for 2-aminoethyl 2-aminoethanethiolsulfonate (Ristey, 1965) and 101° for *N,N*-diglycyl-L-cystine dihydrate (Yakel & Hughes, 1954).

The author wishes to thank Dr Isabella Karle for both her interest and constructive comments throughout the course of this work. He is also indebted to Mr Stephen Brenner who prepared many of the programs used.

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Crystal data of two high pressure phases of SrB₂O₄. By P. D. DERNIER, *Bell Telephone Laboratories, Inc., Murray Hill, New Jersey, U.S.A.*

$SrB_2O_4(III)$ and $SrB_2O_4(IV)$ are two high pressure phases of strontium metaborate. Polycrystalline $SrB_2O_4(III)$ was prepared at 15 kbar and 600°C. It is orthorhombic, with $a = 12·426 \pm 0·002$, $b = 6·418 \pm 0·001$ and $c = 11·412 \pm 0·002$ Å, $Z = 12$, $d_c = 3·77$ g.cm⁻³, symmetry $Pna2_1$, and is isostructural with $CaB_2O_4(III)$. $SrB_2O_4(IV)$, formed at 20 kbar and 600°C, is cubic, with $a = 9·222 \pm 0·001$ Å, $Z = 12$, $d_c = 4·38$ g.cm⁻³, space group symmetry $Pa3$, and is isostructural with $CaB_2O_4(IV)$. In general the behavior of SrB_2O_4 under pressure is very similar to that of CaB_2O_4.

Introduction

This paper reports the synthesis and crystal data of two new high pressure phases of strontium metaborate. At atmospheric pressure SrB_2O_4 is isostructural with $CaB_2O_4(I)$ (Block, Perloff & Weir, 1964). The latter compound is orthorhombic with all boron atoms triangularly coordinated and the calcium atoms surrounded by eight-oxygen polyhedra. Since the polymorphism of SrB_2O_4 is similar to that of CaB_2O_4, all modifications of SrB_2O_4 will be designated in the same fashion as their isostructural CaB_2O_4 counterparts. (Marezio, Remeika, & Dernier, 1969a).

Synthesis

The high pressure apparatus and experimental procedures were the same as has been previously described in the synthesis of the high pressure modifications of CaB_2O_4 (Marezio et al. 1969 a, b). However, the pressure and temperature conditions were significantly lower for each of the respective high pressure phases of SrB_2O_4. $SrB_2O_4(III)$ was retained metastably after pressurizing $SrB_2O_4(I)$ to 15 kbar and raising the temperature to 600°C for a one hour period. The synthesis of $SrB_2O_4(IV)$ required a pressure of 20 kbar and a temperature of 600°C. Further increases of pressure above 40 kbar resulted in the decomposition of SrB_2O_4. One product of decomposition was found to be SrB_4O_7 (Krogh-Moe, 1964), as identified by X-ray powder photographs and precession films.

Both $SrB_2O_4(III)$ and $SrB_2O_4(IV)$ could be reconverted to the low pressure starting material, $SrB_2O_4(I)$, by annealing overnight at 750°C in air. X-ray powder films of the annealed SrB_2O_4 and unpressurized SrB_2O_4 were identical. In addition, single crystals of both high pressure modifications were grown at a pressure of 15 kbar and a temperature of 600°C with water as a solvent. The crystals were easily identified and separated under a crossed polarized field of light, since the crystals of $SrB_2O_4(III)$ were birefringent whereas those of $SrB_2O_4(IV)$ were isotropic. It should be noted that the presence of water apparently lowered the pressure range of stability of $SrB_2O_4(IV)$. This phenomenon has been observed previously for several other systems but no *a priori* justification can be proposed at this time.

Crystal data

From precession photographs taken with Mo $K\alpha$ radiation $SrB_2O_4(III)$ was found to be orthorhombic with systematic absences for $0kl$, $k + l = 2n + 1$, and for $h0l$, $h = 2n + 1$. These are identical with the conditions found for $CaB_2O_4(III)$ (Marezio, Remeika & Dernier, 1969a). The correct space group for $CaB_2O_4(III)$ was found to be $Pna2_1$ and it is highly probable that it is the same for $SrB_2O_4(III)$. The lattice parameters for $SrB_2O_4(III)$ were