

|      |             |             |             |        |
|------|-------------|-------------|-------------|--------|
| C(4) | 0.41246 (9) | 0.0897 (5)  | 0.8925 (1)  | 0.0270 |
| C(5) | 0.45048 (9) | 0.0313 (6)  | 0.8242 (1)  | 0.0365 |
| C(6) | 0.40629 (9) | 0.3088 (6)  | 1.0132 (1)  | 0.0298 |
| C(7) | 0.32392 (9) | 0.0590 (6)  | 0.9657 (1)  | 0.0317 |
| N(3) | 0.43879 (7) | 0.2502 (5)  | 0.94972 (9) | 0.0295 |
| N(4) | 0.43475 (8) | 0.4759 (6)  | 1.06836 (9) | 0.0366 |
| N(5) | 0.40831 (9) | 0.5722 (6)  | 1.1375 (1)  | 0.0449 |
| N(6) | 0.34892 (7) | 0.2158 (5)  | 1.02451 (9) | 0.0338 |
| O(1) | 0.34194 (7) | -0.2608 (5) | 0.77594 (9) | 0.0496 |

| Compound (3) |            |            |            |        |
|--------------|------------|------------|------------|--------|
| C(1)         | 0.7559 (4) | 0.7053 (4) | 1.1558 (5) | 0.0295 |
| C(2)         | 0.7444 (6) | 0.6990 (5) | 1.3757 (5) | 0.0439 |
| C(3)         | 0.7203 (4) | 0.8379 (4) | 1.0322 (4) | 0.0271 |
| C(4)         | 0.7904 (4) | 1.0112 (4) | 1.0718 (5) | 0.0265 |
| C(5)         | 0.9074 (5) | 1.0835 (4) | 1.2512 (5) | 0.0378 |
| C(6)         | 0.6661 (4) | 1.0713 (4) | 0.7808 (5) | 0.0284 |
| C(7)         | 0.6186 (4) | 0.7965 (4) | 0.8553 (5) | 0.0318 |
| N(1)         | 0.8383 (4) | 0.4739 (4) | 1.1802 (5) | 0.0425 |
| N(2)         | 0.7933 (4) | 0.5946 (3) | 1.0657 (4) | 0.0342 |
| N(3)         | 0.7621 (4) | 1.1268 (3) | 0.9492 (4) | 0.0294 |
| N(4)         | 0.6444 (4) | 1.1863 (4) | 0.6489 (4) | 0.0394 |
| N(5)         | 0.7256 (5) | 1.3625 (4) | 0.6728 (5) | 0.0475 |
| N(6)         | 0.5883 (4) | 0.9079 (4) | 0.7296 (4) | 0.0329 |

Table 2. Selected geometric parameters (Å, °)

| Compound (2)   |           |                |           |
|----------------|-----------|----------------|-----------|
| C(1)—C(2)      | 1.505 (3) | C(4)—N(3)      | 1.325 (2) |
| C(1)—C(3)      | 1.475 (3) | C(6)—N(3)      | 1.358 (2) |
| C(1)—O(1)      | 1.219 (2) | C(6)—N(4)      | 1.332 (3) |
| C(3)—C(4)      | 1.421 (3) | C(6)—N(6)      | 1.350 (2) |
| C(3)—C(7)      | 1.387 (3) | C(7)—N(6)      | 1.327 (3) |
| C(4)—C(5)      | 1.497 (3) | N(4)—N(5)      | 1.410 (2) |
| C(3)—C(1)—C(2) | 118.5 (2) | N(3)—C(4)—C(5) | 115.7 (2) |
| O(1)—C(1)—C(2) | 119.0 (2) | N(4)—C(6)—N(3) | 115.5 (2) |
| O(1)—C(1)—C(3) | 122.4 (2) | N(6)—C(6)—N(3) | 126.2 (2) |
| C(4)—C(3)—C(1) | 124.0 (2) | N(6)—C(6)—N(4) | 118.4 (2) |
| C(7)—C(3)—C(1) | 120.6 (2) | N(6)—C(7)—C(3) | 125.8 (2) |
| C(7)—C(3)—C(4) | 115.4 (2) | C(6)—N(3)—C(4) | 118.1 (2) |
| C(5)—C(4)—C(3) | 123.7 (2) | N(5)—N(4)—C(6) | 124.2 (2) |
| N(3)—C(4)—C(3) | 120.6 (2) | C(7)—N(6)—C(6) | 114.0 (2) |
| Compound (3)   |           |                |           |
| C(1)—C(2)      | 1.508 (5) | C(6)—N(3)      | 1.344 (4) |
| C(1)—C(3)      | 1.472 (4) | C(6)—N(4)      | 1.345 (4) |
| C(1)—N(2)      | 1.279 (4) | C(6)—N(6)      | 1.348 (4) |
| C(3)—C(4)      | 1.402 (4) | C(7)—N(6)      | 1.323 (4) |
| C(3)—C(7)      | 1.394 (4) | N(1)—N(2)      | 1.392 (4) |
| C(4)—C(5)      | 1.501 (4) | N(4)—N(5)      | 1.407 (4) |
| C(4)—N(3)      | 1.330 (4) |                |           |
| C(3)—C(1)—C(2) | 121.5 (3) | N(4)—C(6)—N(3) | 118.4 (3) |
| N(2)—C(1)—C(2) | 122.2 (3) | N(6)—C(6)—N(3) | 125.7 (3) |
| N(2)—C(1)—C(3) | 116.2 (3) | N(6)—C(6)—N(4) | 115.9 (3) |
| C(4)—C(3)—C(1) | 124.9 (3) | N(6)—C(7)—C(3) | 124.5 (3) |
| C(7)—C(3)—C(1) | 120.2 (3) | N(1)—N(2)—C(1) | 117.3 (3) |
| C(7)—C(3)—C(4) | 114.9 (3) | C(6)—N(3)—C(4) | 117.1 (3) |
| C(5)—C(4)—C(3) | 123.6 (3) | N(5)—N(4)—C(6) | 123.4 (3) |
| N(3)—C(4)—C(3) | 122.3 (3) | C(7)—N(6)—C(6) | 115.4 (3) |
| N(3)—C(4)—C(5) | 114.1 (3) |                |           |

The structure was solved using direct methods and successive Fourier maps (SHELXS86; Sheldrick, 1985), and refined using CRYSTALS (Watkin, Carruthers & Betteridge, 1985). H atoms were located from difference syntheses.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1062). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 2-Acetyl-3-methyl-4H-1,4-benzothiazine 1-Oxide

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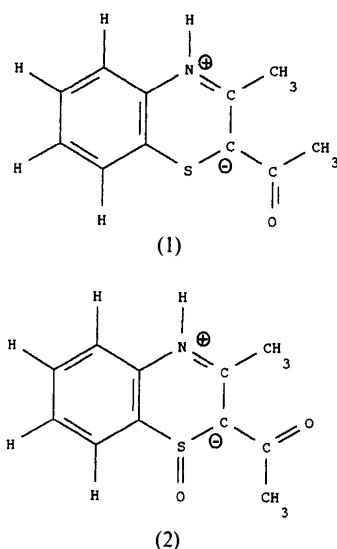
(Received 6 August 1993; accepted 11 February 1994)

## Abstract

Crystals of the title compound 2-acetyl-3-methyl-4H-1,4-benzothiazine 1-oxide (2), C<sub>11</sub>H<sub>11</sub>NO<sub>2</sub>S, crystallize in the monoclinic space group *P*<sub>2</sub><sub>1</sub>/*n*. The cell parameters are almost identical to those of the unoxidized precursor 2-acetyl-3-methyl-4H-1,4-benzothiazine (1). The change in molecular geometry of the acetyl group with respect to the ring moiety in (2) from that in (1) is a consequence of hydrogen bonding involving the sulfoxide O atom.

**Comment**

The structural determination of the title compound was carried out as part of a study of complexes of tin with compounds containing N and S heteroatoms which have a variety of industrial uses and show promise as herbicides as well as in pharmacological applications (Brown & Davidson, 1985). Crystals of compound (1) were obtained by mixing 2-aminothiophenol with acetylacetone and refluxing the reaction mixture overnight. The crystal structure of this compound, synthesized by a different method, had been determined previously (Ferguson & Ruhl, 1982). The reaction of  $\text{Me}_2\text{SnCl}_2$  with (1), carried out under basic conditions (using sodium methoxide), yielded thick brown needles of compound (2). Although it is known that  $\text{Me}_2\text{SnCl}_2$  aided the autoxidation of (1), its exact role is still unclear.



The title compound is composed of planar zwitterions with conjugated double bonds throughout the molecule giving rise to the intense brown colour. The acetyl O atom is *trans* to the S atom and is not

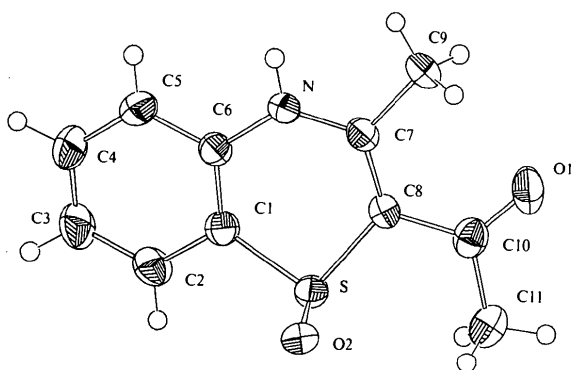


Fig. 1. A perspective drawing of compound (2) with displacement ellipsoids drawn at the 50% probability level.

involved in hydrogen bonding, as is also the case for compound (1). Hydrogen bonds exist between the NH groups and the sulfoxide O atoms of each pair of centrosymmetrically related molecules [ $\text{O}2 \cdots \text{N}^i = 2.780(5)$ ,  $\text{O}2 \cdots \text{H}5^i = 1.9 \text{ \AA}$ ; symmetry code: (i)  $1 - x, -y, 1 - z$ ].

The atomic numbering scheme and hydrogen-bonding scheme are illustrated in Figs. 1 and 2, respectively.

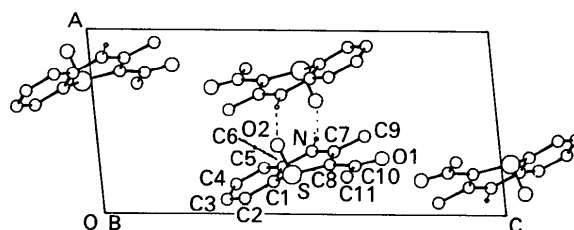


Fig. 2. Packing diagram showing the intermolecular hydrogen bonds in the unit cell.

**Experimental***Crystal data*

$\text{C}_{11}\text{H}_{11}\text{NO}_2\text{S}$

$M_r = 221.28$

Monoclinic

$P2_1/n$

$a = 7.763(1) \text{ \AA}$

$b = 7.751(1) \text{ \AA}$

$c = 17.071(4) \text{ \AA}$

$\beta = 96.26(2)^\circ$

$V = 1021.0(3) \text{ \AA}^3$

$Z = 4$

$D_x = 1.439 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 13\text{--}14^\circ$

$\mu = 0.28 \text{ mm}^{-1}$

$T = 300 \text{ K}$

Thick needle

$0.3 \times 0.3 \times 0.3 \text{ mm}$

Brown

*Data collection*

Enraf-Nonius CAD-4 diffractometer

$\omega$ - $2\theta$  scans

Absorption correction:

empirical (DIFABS; Walker & Stuart, 1983)

$T_{\min} = 0.967$ ,  $T_{\max} = 0.998$

2090 measured reflections

1784 independent reflections

1267 observed reflections

$[I > 3\sigma(I)]$

$\theta_{\max} = 25^\circ$

$h = 0 \rightarrow 9$

$k = 0 \rightarrow 9$

$l = -20 \rightarrow 20$

3 standard reflections monitored every 400 reflections

intensity variation:  $-0.204\% \text{ h}^{-1}$

*Refinement*

Refinement on  $F$

$R = 0.041$

$wR = 0.047$

$S = 0.75$

1267 reflections

136 parameters

H-atom parameters not refined

$w = 1/[\sigma^2(F) + (0.02F)^2 + 1]$

$(\Delta/\sigma)_{\max} = 0.19$

$\Delta\rho_{\max} = 0.633 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.238 \text{ e \AA}^{-3}$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)
$$B_{\text{eq}} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j.$$

|     | x          | y           | z           | B <sub>eq</sub> |
|-----|------------|-------------|-------------|-----------------|
| S   | 0.2170 (1) | 0.2592 (1)  | 0.47641 (5) | 2.64 (2)        |
| O1  | 0.3103 (4) | 0.2810 (4)  | 0.7043 (2)  | 4.35 (7)        |
| O2  | 0.3783 (3) | 0.3343 (3)  | 0.4467 (2)  | 3.02 (5)        |
| N   | 0.3482 (4) | -0.1015 (4) | 0.5317 (2)  | 2.49 (6)        |
| C1  | 0.1798 (5) | 0.0591 (5)  | 0.4278 (2)  | 2.55 (7)        |
| C2  | 0.0876 (5) | 0.0632 (6)  | 0.3526 (2)  | 3.31 (8)        |
| C3  | 0.0810 (6) | -0.0814 (6) | 0.3067 (2)  | 3.92 (9)        |
| C4  | 0.1639 (5) | -0.2306 (6) | 0.3341 (2)  | 3.85 (9)        |
| C5  | 0.2525 (5) | -0.2376 (5) | 0.4083 (2)  | 3.08 (8)        |
| C6  | 0.2601 (5) | -0.0917 (5) | 0.4557 (2)  | 2.43 (7)        |
| C7  | 0.3461 (4) | 0.0211 (5)  | 0.5871 (2)  | 2.37 (7)        |
| C8  | 0.2740 (5) | 0.1827 (5)  | 0.5731 (2)  | 2.47 (7)        |
| C9  | 0.4304 (5) | -0.0371 (5) | 0.6662 (2)  | 3.09 (8)        |
| C10 | 0.2677 (5) | 0.3131 (5)  | 0.6352 (2)  | 2.88 (8)        |
| C11 | 0.2082 (7) | 0.4916 (6)  | 0.6126 (3)  | 4.6 (1)         |

Table 2. Selected geometric parameters (Å, °)

|          |           |            |           |
|----------|-----------|------------|-----------|
| S—O2     | 1.517 (3) | C2—C3      | 1.365 (6) |
| S—C1     | 1.768 (4) | C3—C4      | 1.380 (6) |
| S—C8     | 1.765 (3) | C4—C5      | 1.375 (5) |
| O1—C10   | 1.216 (4) | C5—C6      | 1.388 (5) |
| N—C6     | 1.402 (4) | C7—C8      | 1.382 (5) |
| N—C7     | 1.342 (4) | C7—C9      | 1.504 (4) |
| C1—C2    | 1.400 (5) | C8—C10     | 1.469 (5) |
| C1—C6    | 1.385 (5) | C10—C11    | 1.496 (5) |
| O2—S—C1  | 106.1 (2) | N—C6—C5    | 118.8 (3) |
| O2—S—C8  | 108.0 (2) | C1—C6—C5   | 119.9 (3) |
| C1—S—C8  | 99.0 (2)  | N—C7—C8    | 123.7 (3) |
| C6—N—C7  | 124.9 (3) | N—C7—C9    | 112.5 (3) |
| S—C1—C2  | 116.9 (3) | C8—C7—C9   | 123.8 (3) |
| S—C1—C6  | 122.3 (3) | S—C8—C7    | 121.5 (3) |
| C2—C1—C6 | 120.0 (3) | S—C8—C10   | 114.8 (3) |
| C1—C2—C3 | 119.4 (4) | C7—C8—C10  | 122.9 (3) |
| C2—C3—C4 | 120.4 (4) | O1—C10—C8  | 122.1 (4) |
| C3—C4—C5 | 120.9 (4) | O1—C10—C11 | 118.9 (4) |
| C4—C5—C6 | 119.3 (4) | C8—C10—C11 | 118.9 (3) |
| N—C6—C1  | 121.3 (3) |            |           |

The structure was solved by the Patterson synthesis method and all H atoms were generated geometrically with C—H 0.95 Å; they were allowed to ride with *B* equal to 1.3 times that of the parent atom. All computer programs used for structure solution and refinement were from the *MolEN* package (Fair, 1990).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HL1049). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Low-Temperature Phase of Tetrapropylammonium Iodide

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## Abstract

The I<sup>-</sup> ion of the title compound, C<sub>12</sub>H<sub>28</sub>N<sup>+</sup>.I<sup>-</sup>, is surrounded by four [(C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N]<sup>+</sup> cationic units and *vice versa*. The distance from the I<sup>-</sup> ion to the nearest N atom is 4.65 Å.

## Comment

Tetraalkylammonium halides (R<sub>4</sub>NX: R = alkyl group; X = halogen) are ionic crystals composed of R<sub>4</sub>N<sup>+</sup> and X<sup>-</sup> ions. In the R<sub>4</sub>N<sup>+</sup> ion, four alkyl chains with the same number of C atoms are joined to the N atom.

Tetraalkylammonium halides can be classified into three groups, each showing a different type of disordering behaviour (Xenopoulos, Cheng, Yasuniwa & Wunderlich, 1992). That is, methyl, ethyl and propyl salts only have orientational disordering transitions, giving plastic crystals with dynamic orientational disorder and long-range positional order. Butyl to heptyl salts may show a combination of orientational and conformational disorder, giving the possibility of both plastic crystals and 'condis' (conformationally disordered) crystals (Wunderlich, Möller, Grebowicz & Baur, 1988), which have dynamic conformational disorder and long-range positional and orientational order. Salts with longer alkyl chains display conformational disordering only.

Structural data give basic information on the phase-transition process. As reliable structure deter-