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Structure of 3,4-Dimethylthiazole-2-thione

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Abstract. $C_5H_7NS_2$, $M_r = 145{\cdot}2$, orthorhombic, $Pna2_1$, $a = 7{\cdot}555\ (4)$, $b = 7{\cdot}513\ (4)$, $c = 12{\cdot}003\ (7)$ Å, $V = 681{\cdot}3\ (7)$ Å^3, $Z = 4$, $D_m = 1{\cdot}42\ (1)$, $D_x = 1{\cdot}42\ (1)$ Mg m^{-3}, $\lambda(\text{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 61{\cdot}3$ mm^{-1}, $F(000) = 304$, $T = 298$ K, final $R = 0{\cdot}069$ for 479 observed independent reflections. The heterocyclic ring is planar and bond distances and angles are mainly as expected, but some C—S and C—N bond distances slightly deviate from the values given in the literature for similar compounds.

Introduction. The reaction of *N*-alkylthiazolium halides with potassium superoxide has recently been reported by Dondoni, Galliani & Mastellari (1985). The reaction products *N*-alkylthiazol-2-one and the corresponding thio-analogue have been characterized by spectroscopic techniques and their structures were assigned on the basis of the X-ray analysis reported in this paper.

Experimental. Crystal 0·55 × 0·46 × 0·28 mm. D_m determined pycnometrically. Orthorhombic, Laue class *mm*2, systematic extinctions $h0l$, $h + l = 2n + 1$, $hk0$, $k = 2n + 1$, space group $Pna2_1$.

Siemens AED diffractometer on-line to a General Automation Jumbo 220 microcomputer, Ni-filtered Cu $K\alpha$ radiation, θ–2θ scan, scan width from $(\theta - 0{\cdot}60)$ to $(\theta + 0{\cdot}60 + 0{\cdot}142 + \tan\theta)^\circ$; scan speed 3·0° min^{-1}. Cell dimensions based on 25 (θ,χ,φ) *hkl* measured intensities. 794 symmetry-independent reflections ($0 \le h \le 8$, $0 \le k \le 9$, $0 \le l \le 14$, $3 \le \theta \le 70^\circ$) collected at $T = 298$ K with a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) procedure. One standard reflection, no significant deviations from the initial intensity. Corrections for Lorentz and polarization, no correction for absorption effects.

Structure solved by direct methods (*MULTAN*, Main, Woolfson, Lessinger, Germain & Declercq, 1974). 479 observed reflections $[I > 2\sigma(I)]$ in full-matrix least-squares refinement; 88 parameters; H(5) from difference electron density map; methyl H atoms were calculated and refined as rigid groups; $\sum w||F_o| - |F_c||^2$ minimized; $w = [\sigma^2(F_o) + 0{\cdot}72245F_o^2]^{-1}$, *SHELX*76 system (Sheldrick, 1976); $(\Delta/\sigma)_{\max} = 0{\cdot}090$, $\Delta\rho = -0{\cdot}43$ to $0{\cdot}91$ e Å^{-3}; the latter was found at

Table 1. *Final atomic coordinates* (×10^4) *and equivalent isotropic temperature factors* (×10^4 Å^2) *of the non-hydrogen atoms with e.s.d.'s in parentheses*

$$U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S1	9201 (4)	4542 (4)	4367	504 (9)
C2	8529 (15)	3829 (24)	3097 (11)	514 (49)
N3	8517 (12)	2034 (19)	3086 (10)	451 (33)
C4	9039 (16)	1195 (22)	4084 (12)	487 (39)
C5	9431 (17)	2371 (23)	4862 (14)	518 (43)
C6	8025 (18)	1006 (26)	2099 (18)	626 (52)
C7	9161 (19)	−767 (24)	4166 (21)	668 (68)
S8	7979 (5)	5206 (6)	2019 (5)	640 (13)

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *with e.s.d.'s in parentheses*

S1—C2	1·694 (14)	N3—C4	1·410 (19)
S1—C5	1·745 (17)	N3—C6	1·462 (24)
C2—N3	1·349 (23)	C4—C5	1·319 (23)
C2—S8	1·708 (16)	C4—C7	1·480 (25)
C2—S1—C5	92·3 (8)	C4—N3—C6	121·6 (13)
S1—C2—S8	124·3 (9)	N3—C4—C7	121·3 (13)
S1—C2—N3	109·1 (9)	N3—C4—C5	111·4 (14)
N3—C2—S8	126·6 (11)	C5—C4—C7	127·3 (15)
C2—N3—C6	122·5 (13)	S1—C5—C4	111·3 (12)
C2—N3—C4	115·9 (12)		
C2—S1—C5—C4	1·0 (13)	C2—N3—C4—C5	0·7 (19)
C5—S1—C2—S8	179·8 (11)	C2—N3—C4—C7	−177·2 (14)
C5—S1—C2—N3	−0·6 (11)	C6—N3—C4—C7	1·8 (22)
S1—C2—N3—C4	0·0 (16)	C6—N3—C4—C5	179·7 (14)
S1—C2—N3—C6	−178·9 (12)	N3—C4—C5—S1	−1·1 (17)
S8—C2—N3—C6	0·7 (21)	C7—C4—C5—S1	176·7 (14)
S8—C2—N3—C4	179·6 (11)		

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0·88 Å from S atom. Final refinement converged to $R = 0{\cdot}069$, $wR = 0{\cdot}071$, five reflections omitted from the last cycle. Scattering factors, f' and f'' from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters are given in Table 1,* bond distances, bond angles and selected torsion angles in Table 2.

The molecule (see Fig. 1) is practically planar; the weighted least-squares plane through the thiazole ring gives $\sum(\Delta/\sigma)^2 = 0{\cdot}834$. C(6) and S(8) also lie in this plane while C(7) shows a small but significant out-of-plane deviation of 0·72 (16) Å.

Bond distances and bond angles clearly show a localized π interaction between C(4)—C(5), according to the distance S(1)—C(5) = 1·745 (17) Å which is close to the expected value for an S—C(sp^2) = 1·74 Å bond (Pauling, 1967).

Other C—S bond distances, C(2)—S(1) = 1·694 (14) and C(2)—S(8) = 1·708 (16) Å, are significantly shorter than the corresponding distances observed in benzothiazoles (Hinrichs, Mandak & Klar, 1982; Zingaro & Meyers, 1980). This seems to be related to the lengthening of the distance N(3)—C(2) = 1·349 (23) Å which is significantly greater than the corresponding ones, 1·317 (17) and 1·277 (5) Å, given by these authors. Other bond distances and bond angles are mainly as expected.

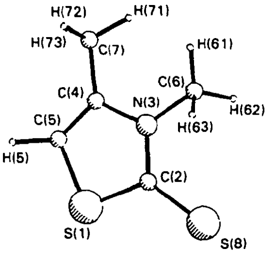

Fig. 1. View of the molecule projected along [100].

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43338 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A New Polymorph of Dibenzoylmethane

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Abstract. 1,3-Diphenyl-1,3-propanedione (dibenzoylmethane), $C_{15}H_{12}O_2$, $M_r = 224{\cdot}3$, orthorhombic, *Pbca*, $a = 11{\cdot}706$ (5), $b = 7{\cdot}668$ (4), $c = 25{\cdot}572$ (8) Å, $V = 2295$ (3) Å^3, $Z = 8$, $D_x = 1{\cdot}298$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 0{\cdot}79$ cm^{-1}, $F(000) = 944$, $T = 298$ K, $R = 0{\cdot}049$ for 915 observed reflections, $wR = 0{\cdot}048$. This polymorph of dibenzoylmethane (DBM) is a metastable kinetically favored crystal form in which the molecules are enolic and contain a slightly asymmetric intramolecular hydrogen bond. The molecular structure is nearly identical to that of DBM molecules in the stable crystal form, but the packing patterns of the two different polymorphs are markedly different.

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