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Studies in Nonlinear Optical Materials: Structure of Methyl 2-(4-Ethyl-5-methyl-2-thioxo-2,3-dihydro-1,3-thiazol-3-yl)propionate

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Abstract. $C_{10}H_{15}NO_2S_2$, $M_r = 245\cdot0$, orthorhombic, $P2_12_12_1$, $a = 6\cdot639$ (2), $b = 8\cdot205$ (2), $c = 22\cdot528$ (6) Å, $V = 1227\cdot2$ (6) Å^3, $Z = 4$, $D_m = 1\cdot315$, $D_x = 1\cdot326$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot7107$ Å, $\mu = 3\cdot63$ cm^{-1}, $F(000) = 520$, $T = 293$ K, $R = 0\cdot037$ for 1115 significant reflections. The second-harmonic-generation (SHG) efficiency of this compound is only 1/10th of the urea standard. The observed low second-order nonlinear response may be attributed to the unfavourable packing of the molecules in the crystal lattice.

Introduction. As part of a long-range research programme on developing organic compounds exhibiting good nonlinear optical properties, the molecular packing of the title compound was investigated. Although the present molecule is not one with a well defined charge-transfer axis such as nitroanilines (Levine, Bethea, Thurmond, Lynch & Bernstein, 1979; Lipscomb, Garito & Narang, 1981) and push–pull ethylenes (Kanagapushpam, Padmanabhan & Venkatesan, 1987), it was considered worth investigating in view of its large ground-state dipole moment ($\sim 30\cdot7 \times 10^{-30}$ Cm) and also because it crystallizes in a non-centrosymmetric space group.

Experimental. Single crystals of the title compound obtained from methanol by slow evaporation, approximate dimensions $0\cdot05 \times 0\cdot45 \times 0\cdot40$ mm. D_m by flotation. Preliminary oscillation and Weissenberg photographs indicated that the crystals were orthorhombic. Lattice parameters refined by a least-squares fit to settings for 25 accurately centred reflections. Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan mode, scan speed 1° min^{-1}, $\theta \leq 25°$. During data collection two standard reflections (219 and 124) showed only statistical fluctuations within ±2%. 1365 reflections collected, *hkl* range *h*: 0 to 7, *k*: 0 to 9, *l*: 0 to 26, 1115 significant, $|F_o| \geq 3\sigma|F_o|$. Data not corrected for absorption. Structure solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement (*SHELX*76; Sheldrick, 1976) of a scale factor, positional and anisotropic thermal parameters for non-H atoms and positional and isotropic thermal parameters for H atoms (all located from difference map) converged to $R = 0\cdot037$, $wR = 0\cdot046$, $S = 1\cdot2$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1\cdot1467/[\sigma^2(F) + 0\cdot001\,127\,|F_o|^2]$. In the final cycles of refinement, Δ/σ for non-H atoms is about $0\cdot02$,

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$\Delta\rho_{\rm max} = +0{\cdot}23$, $\Delta\rho_{\rm min} = -0{\cdot}25$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).*

Discussion. The atomic positional and thermal parameters for non-H atoms are listed in Table 1. Bond lengths and angles are presented in Table 2.

The bond lengths and angles in the 2,3-dihydro-1,3-thiazole-2-thione ring agree well with those found in 3,4-diisopropyl-2,3-dihydro-1,3-thiazole-2-thione (Pèpe & Pierrot, 1976*a*) and 3,4-diisopropyl-5-methyl-2,3-dihydro-1,3-thiazole-2-thione (Pèpe & Pierrot, 1976*b*). The five-membered ring is planar within experimental limits with atoms S(6), C(7), C(8) and C(10) deviating −0·065 (2), 0·090 (5), 0·026 (4) and 0·021 (4) Å respectively from the plane. The torsion angles C(2)—N(3)—C(10)—C(12) and N(3)—C(10)—C(12)—O(14) are −56·7 (5) and −38·1 (5)°, respectively. In this conformation, the N(3)···O(14) distance is as short as 2·693 (3) Å.

The packing of the molecules in the unit cell is shown in Fig. 1. The intermolecular S(1)···S(1$^{\rm i}$) [(i): $\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$] distance of 3·646 (2) Å is slightly shorter than the van der Waals sum of 3·70 Å (Pauling, 1960). Guru Row & Parthasarathy (1981) surveyed 57 structures containing S···S intermolecular contacts ≤3·70 Å; on the basis of θ_i, φ_i, θ_j and φ_j values, they found that the majority of these contacts correspond to electrophile–nucleophile pairing involving the HOMO of one S atom and the LUMO of the other. In this crystal structure, S(1$^{\rm i}$) is an electrophile ($\theta_i = 19{\cdot}0$, $\varphi_i = 168{\cdot}7°$), whereas S(1) is a nucleophile ($\theta_j = 66{\cdot}8$, $\varphi_j = 173{\cdot}2°$).

The SHG (second-harmonic-generation) efficiency of the powder sample was measured by Eaton & Wang (1986) and was found to be only 1/10th of that of the

Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3) *for non-*H *atoms*

E.s.d.'s are given in parentheses. $U_{\rm eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
S(1)	9635 (2)	2331 (1)	5329 (1)	42 (1)
C(2)	8392 (6)	3305 (5)	5897 (2)	37 (1)
N(3)	7148 (4)	2243 (3)	6165 (1)	35 (1)
C(4)	7171 (6)	649 (4)	5933 (2)	36 (1)
C(5)	8447 (6)	501 (5)	5473 (2)	39 (1)
S(6)	8808 (2)	5248 (1)	6075 (1)	53 (1)
C(7)	8807 (9)	−947 (6)	5080 (2)	54 (1)
C(8)	5859 (6)	−674 (5)	6171 (2)	46 (1)
C(9)	3696 (8)	−608 (7)	5942 (3)	62 (2)
C(10)	5854 (6)	2737 (5)	6665 (2)	43 (1)
C(11)	4130 (8)	3847 (8)	6474 (3)	63 (2)
C(12)	7085 (7)	3459 (5)	7176 (2)	50 (1)
O(13)	6491 (6)	4506 (4)	7497 (1)	69 (1)
O(14)	8815 (5)	2663 (4)	7244 (1)	55 (1)
C(15)	10114 (10)	3231 (9)	7719 (2)	76 (2)

Table 2. *Selected bond distances* (Å) *and angles* (°) *involving non-*H *atoms with their e.s.d.'s in parentheses*

S(1)—C(2)	1·720 (4)	C(5)—C(7)	1·501 (6)
S(1)—C(5)	1·727 (4)	C(8)—C(9)	1·527 (7)
C(2)—N(3)	1·344 (5)	C(10)—C(11)	1·525 (7)
C(2)—S(6)	1·667 (4)	C(10)—C(12)	1·531 (6)
N(3)—C(4)	1·409 (4)	C(12)—O(13)	1·190 (5)
N(3)—C(10)	1·473 (5)	C(12)—O(14)	1·330 (6)
C(4)—C(5)	1·344 (6)	O(14)—C(15)	1·451 (6)
C(4)—C(8)	1·491 (6)		
C(2)—S(1)—C(5)	92·6 (2)	S(1)—C(5)—C(7)	120·3 (3)
S(1)—C(2)—N(3)	109·1 (3)	C(4)—C(5)—C(7)	128·8 (4)
S(1)—C(2)—S(6)	123·0 (3)	C(4)—C(8)—C(9)	113·7 (4)
N(3)—C(2)—S(6)	127·9 (3)	N(3)—C(10)—C(11)	112·7 (4)
C(2)—N(3)—C(4)	115·4 (3)	N(3)—C(10)—C(12)	111·7 (3)
C(2)—N(3)—C(10)	121·6 (3)	C(11)—C(10)—C(12)	112·4 (4)
C(4)—N(3)—C(10)	123·1 (3)	C(10)—C(12)—O(13)	124·0 (4)
N(3)—C(4)—C(5)	112·1 (3)	C(10)—C(12)—O(14)	110·9 (4)
N(3)—C(4)—C(8)	122·4 (3)	O(13)—C(12)—O(14)	124·8 (4)
C(5)—C(4)—C(8)	125·4 (4)	C(12)—O(14)—C(15)	116·1 (4)
S(1)—C(5)—C(4)	110·7 (3)		

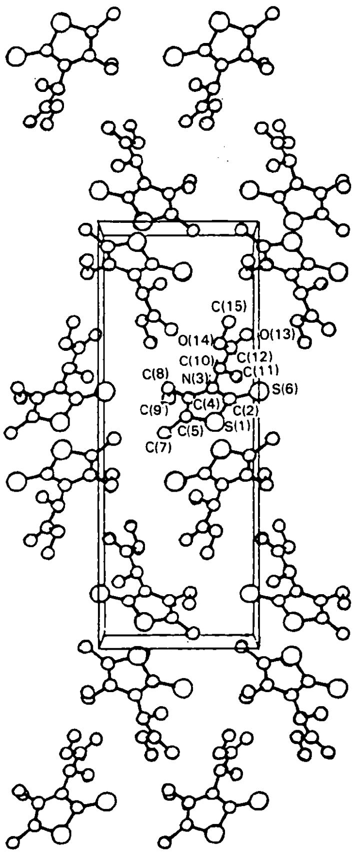

Fig. 1. Packing of the molecules viewed down the *a* axis, *b* axis horizontal, *c* axis vertical.

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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 43915 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.