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Structure of Trimethyl 1-Methyl-3,4,5-pyrazoletricarboxylate, $C_{10}H_{12}N_2O_6$

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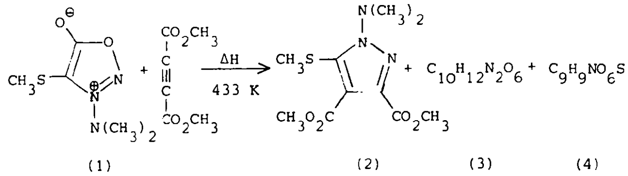
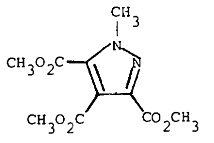
Abstract. $M_r = 256{\cdot}2$, monoclinic, $P2_1/n$, $a = 7{\cdot}773$ (1), $b = 9{\cdot}671$ (1), $c = 16{\cdot}395$ (2) Å, $\beta = 98{\cdot}81$ (1)°, $U = 1217{\cdot}9$ Å^3, $Z = 4$, $D_m = 1{\cdot}39$, $D_x = 1{\cdot}397$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}076$ mm^{-1}. Final $R = 0{\cdot}035$ based on 1295 observed reflections. The analysis has established the chemical structure of the title compound.

Introduction. Reaction of 3-dimethylamino-4-methylthiosydnone (1) with dimethyl acetylenedicarboxylate at 433 K leads to formation of dimethyl 1-dimethylamino-5-methylthio-3,4-pyrazoledicarboxylate (2) and dimethyl 5-methylthio-6-oxo-6*H*-1,2-oxazine-3,4-dicarboxylate (4) together with a compound of the formula $C_{10}H_{12}N_2O_6$ (3) (Gotthardt & Reiter, 1981).



(1) (2) (3) (4)

This formula (3) implied elimination of a methylthio group and an N atom from the primarily formed [3 + 2] cycloadduct of the reactants. Since spectroscopic data and a hydrolysis experiment did not clearly define the constitution of (3), recourse was made to X-ray crystallography which showed (3) to be the unexpected title compound. A report of the preparation of this compound has been made (Gotthardt & Reiter, 1981).



(3)

Experimental. Title compound crystallized from methanol as colorless needles, Weissenberg and precession photographs revealed the systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$, uniquely defining space group $P2_1/n$, lattice constants determined from Bragg angles of 75 reflections centered on a CAD-4 diffractometer, intensities ($\theta \leq 25°$) collected by ω–2θ scans; of 2346 reflections measured, 1295 having $I \geq 2\,\sigma(I)$ used to refine structure which was solved by direct methods (Sheldrick, 1976), large-block least-squares refinement, function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma^2(|F_o|) + 0{\cdot}0009 \times |F_o|^2]$, $F(000) = 536$, neutral-atom scattering factors employed for non-H atoms (Cromer & Waber, 1965), those of Stewart, Davidson & Simpson (1965) for H; refinement with non-H atoms anisotropic and H atoms isotropic converged with $R = 0{\cdot}035$ and $R_w = 0{\cdot}044$, final difference map contained no peak greater than 0·2e Å^{-3}.

Discussion. The final coordinates of the non-H atoms are given in Table 1,* the numbering scheme being defined in Fig. 1. Bond distances and angles are given in Table 2.

Table 1. *Positional* (×10^4) *and equivalent isotropic thermal* (Å^2 ×10^3) *parameters for the non-*H *atoms of* (3) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	$U_{\rm eq}$
N(1)	1822 (2)	6797 (2)	161 (1)	49 (1)
N(2)	2557 (2)	5598 (2)	429 (1)	46 (1)
O(1)	3521 (2)	2726 (2)	−794 (1)	61 (1)
O(2)	379 (2)	3821 (2)	−1896 (1)	52 (1)
O(3)	−287 (2)	7491 (2)	−1879 (1)	63 (1)
O(4)	426 (2)	8931 (2)	−810 (1)	60 (1)
O(5)	2486 (2)	5135 (2)	−2277 (1)	63 (1)
O(6)	3703 (3)	2703 (2)	570 (1)	85 (1)
C(1)	1820 (2)	5323 (2)	−915 (1)	40 (1)
C(2)	1624 (3)	4770 (2)	−1772 (1)	42 (1)
C(3)	2590 (3)	4678 (2)	−199 (1)	42 (1)
C(4)	1365 (3)	6639 (2)	−657 (1)	43 (1)
C(5)	415 (3)	7720 (2)	−1187 (1)	48 (1)
C(6)	3323 (3)	3274 (2)	−76 (1)	51 (1)
C(7)	115 (4)	3158 (3)	−2701 (1)	64 (2)
C(8)	3224 (3)	5421 (3)	1311 (1)	56 (1)
C(9)	−513 (4)	10042 (3)	−1278 (2)	74 (2)
C(10)	4215 (4)	1334 (3)	−792 (2)	80 (2)

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38233 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

N(2)–N(1)	1·338 (3)	C(5)–O(3)	1·202 (3)
N(2)–C(3)	1·364 (3)	C(5)–O(4)	1·323 (3)
N(2)–C(8)	1·470 (3)	C(9)–O(4)	1·451 (3)
N(1)–C(4)	1·343 (3)	C(2)–O(5)	1·195 (3)
C(4)–C(1)	1·403 (3)	C(2)–O(2)	1·326 (3)
C(4)–C(5)	1·483 (3)	C(7)–O(2)	1·453 (3)
C(1)–C(3)	1·382 (3)	C(6)–O(6)	1·191 (3)
C(1)–C(2)	1·490 (3)	C(6)–O(1)	1·321 (3)
C(3)–C(6)	1·474 (3)	C(10)–O(1)	1·450 (3)
C(3)–N(2)–C(8)	128·5 (2)	C(4)–C(5)–O(3)	122·5 (2)
C(3)–N(2)–N(1)	112·0 (2)	C(4)–C(5)–O(4)	112·5 (2)
N(1)–N(2)–C(8)	119·5 (2)	O(3)–C(5)–O(4)	125·0 (2)
N(2)–N(1)–C(4)	105·3 (2)	C(5)–O(4)–C(9)	116·2 (2)
N(1)–C(4)–C(1)	111·4 (2)	C(1)–C(2)–O(5)	124·1 (2)
N(1)–C(4)–C(5)	122·5 (2)	C(1)–C(2)–O(2)	111·1 (2)
C(1)–C(4)–C(5)	126·1 (2)	O(5)–C(2)–O(2)	124·8 (2)
C(4)–C(1)–C(3)	104·4 (2)	C(2)–O(2)–C(7)	116·3 (2)
C(4)–C(1)–C(2)	128·0 (2)	C(3)–C(6)–O(6)	125·9 (2)
C(3)–C(1)–C(2)	127·5 (2)	C(3)–C(6)–O(1)	110·1 (2)
C(1)–C(3)–N(2)	107·0 (2)	O(6)–C(6)–O(1)	124·0 (2)
C(1)–C(3)–C(6)	129·7 (2)	C(6)–O(1)–C(10)	117·7 (2)
N(2)–C(3)–C(6)	123·3 (2)		

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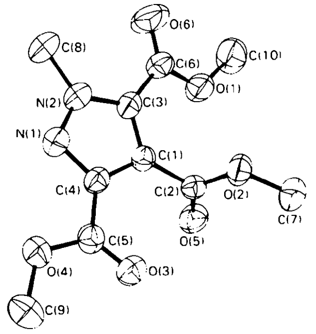

Fig. 1. *ORTEP* drawing (Johnson, 1965) showing 50% probability thermal ellipsoids for trimethyl 1-methyl-3,4,5-pyrazoletricarboxylate (3). H atoms have been omitted.

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2,6-Dithia[7]paracyclophan, $C_{11}H_{14}S_2$, und 2,6,15,19-Tetrathia[7.7]paracyclophan, $C_{22}H_{28}S_4$

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Abstract. $C_{11}H_{14}S_2$: $M_r = 210{\cdot}4$, monoclinic, $P2_1/n$, $a = 6{\cdot}886\ (1)$, $b = 10{\cdot}852\ (3)$, $c = 14{\cdot}461\ (6)$ Å, $\beta = 90{\cdot}34\ (3)°$, $V = 1080{\cdot}53$ Å^3, $Z = 4$, $D_x = 1{\cdot}293$, $D_m = 1{\cdot}31$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}426$ mm^{-1}, $F(000) = 448$, $R_w = 0{\cdot}035$ for 888 observed reflections ($R = 0{\cdot}075$); $C_{22}H_{28}S_4$: $M_r = 420{\cdot}7$, monoclinic, $P2_1/n$, $a = 12{\cdot}057\ (3)$, $b = 5{\cdot}589\ (1)$, $c = 16{\cdot}215\ (5)$ Å, $\beta = 92{\cdot}74\ (2)°$, $Z = 2$, $V = 1091{\cdot}38$ Å^3, $D_x = 1{\cdot}28$, $D_m = 1{\cdot}30$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}422$ mm^{-1}, $F(000) = 448$, $R_w = 0{\cdot}034$ for 1456 observed reflections ($R = 0{\cdot}070$). In the former a benzene ring is substituted by a 1,3-dithiapropane chain in the 1,4 position. The latter molecule, which is formally the dimer of the former, has a center of symmetry with two dithiapropane chains connecting two benzene rings.

Einleitung. Mitchell & Boekelheide (1969) sowie Vögtle (1970) erhielten durch Cyclisierung von 1,4-Bis(brommethyl)benzol mit 1,3-Propandithiol unter Anwendung des Verdünnungsprinzips 2,6,15,19-Tetrathia[7.7]paracyclophan (TTPH,I). Haenel (1977) konnte bei der gleichen Umsetzung neben (I) auch noch 2,6-Dithia[7]paracyclophan (DTPH,II) isolieren und charakterisieren. Vor allem (I) war von uns hinsichtlich

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