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Structure of 5-(3-Methyl-1,2,4-oxadiazole)carbaldehyde Phenylhydrazone

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Abstract. $C_{10}H_{10}N_4O$, $M_r = 202{\cdot}2$, orthorhombic, *Pbca*, $a = 22{\cdot}990$ (6), $b = 10{\cdot}752$ (4), $c = 8{\cdot}172$ (4) Å, $Z = 8$, $U = 2020$ Å^3, $D_m = 1{\cdot}33$ (flotation), $D_x = 1{\cdot}330$ Mg m^{-3}, $T = 298$ K, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 7·15 cm^{-1}, $F(000) = 848$, $R = 0{\cdot}0696$ ($wR = 0{\cdot}0782$) for 624 observed reflections. The whole molecule is essentially planar, which can be seen from the values of the torsion angles about the non-rigid bonds, and the molecular dimensions are in agreement with those found in analogous compounds. The crystal packing is determined by van der Waals forces and none of the intermolecular contacts are shorter than the sum of relevant van der Waals radii.

Experimental. Single crystals obtained by slow evaporation of a solution in absolute ethanol, under reduced constant pressure in a dry atmosphere; approximate unit-cell parameters from preliminary Weissenberg and precession photographs, crystal ~0·2 × 0·2 × 0·08 mm, Philips PW 1100 four-circle diffractometer, graphite monochromator; accurate unit-cell parameters and crystal-orientation matrices (with e.s.d.'s) from least-squares refinement of the 2θ, ω, χ and φ values of 20 carefully centred reflections ($19 < \theta < 25°$); θ–2θ scan, scan speed 0·02° s^{-1}, scan width 1·00°, 2θ range 4–92°; $0 \le h \le 21$, $0 \le k \le 10$, $0 \le l \le 7$. Two standard reflections (231, $\bar{2}3\bar{1}$) monitored every 180 min, no significant variation; 817 reflections measured, 624 with $I \ge 3\sigma(I)$, Lorentz and polarization corrections applied, absorption and extinction corrections ignored; intensities placed on an absolute scale by Wilson's method, trial structure obtained by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Because the data-to-parameter ratio is barely 5:1, it seemed to us convenient to refine the structure by block-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1{\cdot}467[\sigma^2(F_o) + 0{\cdot}0064F_o^2]^{-1}$; adequacy of the weighting scheme confirmed by analysis of the variation of the mean $w(|F_o| - |F_c|)^2$ with $|F_o|$ and $(\sin\theta)/\lambda$, scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 71–103). The refinement was carried out allowing all non-H atoms to vibrate anisotropically; all the H atoms were located from a difference Fourier map and isotropically refined in the last least-squares cycle. Final conventional $R = 0{\cdot}0696$ ($wR = 0{\cdot}0782$) for the 624 observed reflections; calculations carried out on the CYBER76 computer of 'CINECA' with *SHELX*76 (Sheldrick, 1976); $(\Delta/\sigma)_{max}$ in final refinement cycle for positional parameters of the non-H atoms 0·11, max. and min. heights in final difference Fourier synthesis ±0·2 e Å^{-3}. It is our contention that this structure determination is on the borderline of acceptable precision, mainly owing to the poor quality of the crystals. Nevertheless since the aim of this work was the determination of the molecular conformation, we believe that our results do warrant presentation.

The final structural parameters are given in Table 1 and interatomic distances and interbond angles with e.s.d.'s are in Table 2. Torsion angles are in Table 3.†

A perspective view of the molecule, with the atom-numbering scheme, is shown in Fig. 1. Therefore the present X-ray analysis unequivocally demonstrates that the product examined is 5-(3-methyl-1,2,4-oxadiazole)carbaldehyde phenylhydrazone.

Related literature. The title compound belongs to a series of substituted hydrazones synthesized and tested from the pharmacological point of view by the late Professor Silvano Rossi (Rossi, 1985).

The hydrazone position of the molecule, *i.e.* from C(1) to C(8) through N(1), N(2) and C(7), is of special interest. The geometry here as it pertains to

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† Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, least-squares planes and distances involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53948 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and temperature factors* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O(1)	5282 (1)	5115 (3)	3144 (4)	44 (1)
N(1)	4108 (2)	3237 (4)	238 (7)	55 (2)
N(2)	4478 (2)	3889 (4)	1181 (7)	45 (2)
N(3)	5709 (2)	5387 (4)	4329 (6)	43 (2)
N(4)	5638 (2)	3315 (4)	4016 (6)	47 (2)
C(1)	3670 (3)	3824 (6)	−625 (8)	43 (3)
C(2)	3296 (3)	3083 (6)	−1560 (8)	53 (2)
C(3)	2867 (3)	3640 (7)	−2467 (9)	64 (3)
C(4)	2788 (2)	4887 (8)	−2468 (10)	66 (3)
C(5)	3158 (3)	5607 (6)	−1536 (9)	56 (3)
C(6)	3598 (2)	5096 (6)	−636 (7)	47 (2)
C(7)	4856 (2)	3255 (5)	1984 (8)	45 (3)
C(8)	5274 (2)	3867 (5)	3051 (8)	42 (2)
C(9)	5893 (2)	4315 (6)	4792 (9)	45 (2)
C(10)	6340 (3)	4134 (6)	6058 (9)	64 (3)

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

C(1)—C(2)	1·399 (10)	N(2)—C(7)	1·285 (7)
C(2)—C(3)	1·371 (10)	C(7)—C(8)	1·455 (8)
C(3)—C(4)	1·353 (11)	C(8)—O(1)	1·344 (6)
C(4)—C(5)	1·379 (10)	O(1)—N(3)	1·410 (5)
C(5)—C(6)	1·366 (9)	N(3)—C(9)	1·285 (8)
C(6)—C(1)	1·378 (9)	N(4)—C(9)	1·379 (8)
N(1)—C(1)	1·382 (8)	N(4)—C(8)	1·294 (7)
N(1)—N(2)	1·345 (7)	C(9)—C(10)	1·471 (9)

N(3)—O(1)—C(8)	104·8 (3)	C(3)—C(4)—C(5)	118·2 (6)
N(2)—N(1)—C(1)	121·0 (5)	C(4)—C(5)—C(6)	121·9 (6)
N(1)—N(2)—C(7)	116·3 (4)	C(1)—C(6)—C(5)	119·5 (6)
O(1)—N(3)—C(9)	104·2 (4)	N(2)—C(7)—C(8)	120·9 (5)
C(8)—N(4)—C(9)	101·4 (5)	N(4)—C(8)—C(7)	125·8 (5)
N(1)—C(1)—C(6)	123·0 (6)	O(1)—C(8)—C(7)	119·6 (4)
N(1)—C(1)—C(2)	117·8 (6)	O(1)—C(8)—N(4)	114·5 (5)
C(2)—C(1)—C(6)	119·2 (6)	N(3)—C(9)—N(4)	115·1 (5)
C(1)—C(2)—C(3)	119·2 (6)	N(4)—C(9)—C(10)	121·1 (5)
C(2)—C(3)—C(4)	122·0 (6)	N(3)—C(9)—C(10)	123·8 (6)

the hydrazone–azo question has been discussed in detail by Pendergrass, Paul & Curtin (1972); they list literature values of bond lengths expected for the two tautomers: N—N, 1·33–1·38 Å; N=N, 1·23–1·28 Å; N—C(amide), 1·30–1·41 Å; N=C, 1·27–1·29 Å. The

Table 3. *Torsion angles* (°) *with e.s.d.'s in parentheses*

N(2)—N(1)—C(1)—C(2)	−179·0 (6)	C(9)—N(4)—C(8)—O(1)	0·5 (6)
N(2)—N(1)—C(1)—C(6)	2·8 (9)	C(8)—N(4)—C(9)—C(10)	178·8 (6)
C(1)—N(1)—N(2)—C(7)	177·4 (5)	C(9)—N(4)—C(8)—C(7)	−176·3 (6)
N(1)—N(2)—C(7)—C(8)	−179·5 (5)	N(1)—C(1)—C(6)—C(5)	179·2 (6)
N(2)—C(7)—C(8)—O(1)	−2·9 (8)	N(1)—C(1)—C(2)—C(3)	−178·2 (6)
N(2)—C(7)—C(8)—N(4)	173·7 (6)	C(2)—C(1)—C(6)—C(5)	1·1 (9)
N(3)—O(1)—C(8)—N(4)	0·0 (6)	C(6)—C(1)—C(2)—C(3)	0·1 (1·0)
N(3)—O(1)—C(8)—C(7)	177·0 (5)	C(1)—C(2)—C(3)—C(4)	1·0 (1·1)
C(8)—O(1)—N(3)—C(9)	−0·5 (5)	C(2)—C(3)—C(4)—C(5)	0·7 (1·1)
O(1)—N(3)—C(9)—C(10)	−178·8 (5)	C(3)—C(4)—C(5)—C(6)	0·5 (1·1)
O(1)—N(3)—C(9)—N(4)	0·9 (6)	C(4)—C(5)—C(6)—C(1)	−1·4 (1·0)
C(8)—N(4)—C(9)—N(3)	−0·9 (7)		

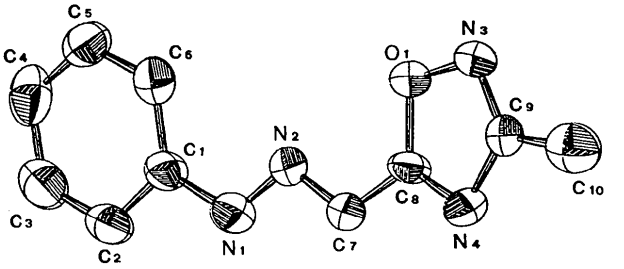

Fig. 1. The molecular structure of the title compound with the atom-numbering scheme.

important point is that our distances fit into the pattern for the hydrazone tautomer. Our N—N distance of 1·345 (7) Å is in the middle of the range quoted while the present N=C distance of 1·285 (7) Å is among the highest values observed in some related compounds.

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3-Isopropyl-2-(4-nitrophenyl)-2,3,4,5-tetrahydro-1,3-oxazine

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Abstract. $C_{13}H_{18}N_2O_3$, $M_r = 250·23$, monoclinic, $P2_1/c$, $a = 11·196$ (2), $b = 16·490$ (3), $c = 7·733$ (1) Å, $\beta = 108·64$ (2)°, $V = 1352·7$ (5) Å^3, $Z = 4$, $D_x = 1·23$ g cm^{-3}, Cu $K\alpha$ radiation, $\lambda = 1·5418$ Å, $\mu = 6·85$ cm^{-1}, $F(000) = 536$, $T = 293$ K, final $R = 0·055$ for 1130 observed reflections. The oxazine ring

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