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Structure of 2-Methyl-5,6,7-triphenyl-6,7-dihydropyrazolo[2,3-*a*]pyrimidine

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Abstract. C₂₅H₂₁N₃, $M_r = 363.46$, monoclinic, $P2_1/n$, $a = 9.245$ (2), $b = 23.502$ (5), $c = 9.340$ (2) Å, $\beta = 103.50$ (3)°, $V = 1973.3$ (2) Å³, $Z = 4$, $D_x = 1.220$ (2) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.068$ cm⁻¹, $F(000) = 768$, $T = 292$ K, $R = 0.091$ for 1442 unique observed reflections. The dihydropyrimidine ring adopts a distorted sofa conformation. The aryl substituents on the saturated C atoms have an axial orientation.

Introduction. Dihydro derivatives of pyrazolo-[1,5-*a*]pyrimidine have high physiological activity, the most important being cardiovascular activity (Tsuda, Mishina, Obata, Inui & Nakamura, 1986). Though chemical and physiological characteristics of these compounds are directly defined by the conformation of their molecules, relevant data on the spatial structure of the dihydropyrazolo[2,3-*a*]pyrimidines are not available. The present paper is a continuation of our investigation of the molecular and crystal structures of dihydropyrazolopyrimidines containing a bridgehead nitrogen (Orlov, Desenko, Potekhin & Struchkov, 1988) and is devoted to an X-ray diffraction study of 2-methyl-5,6,7-triphenyl-6,7-dihydropyrazolo[2,3-*a*]pyrimidine (I).

Experimental. The title compound was prepared by the method described by Orlov, Quiroga, Kolos & Desenko, (1988). Crystals of (I) as pale-yellow plates of approximate dimensions 0.10 × 0.15 × 0.20 mm,

suitable for an X-ray study, were grown from a 2-propanol solution by slow evaporation of the solvent. A Siemens P3/PC diffractometer with graphite-monochromated Mo $K\alpha$ radiation was used. The unit-cell parameters were determined by least-squares fit of setting angles of 9 automatically centred reflections ($24 < \theta < 26^\circ$). The $\theta/2\theta$ scan technique with a variable scan speed (2.0 to 30.0° min⁻¹) was used. Two check reflections were monitored after every 50 measurements and they showed no systematic variation in intensity. 2775 reflections up to $2\theta = 56.0^\circ$ were measured including the check and equivalent reflections, with $0 < h < 12$, $0 < k < 26$, $-11 < l < 11$. Of 2640 unique reflections ($R_{\text{int}} = 0.023$), 2467 reflections had $I > 2\sigma(I)$. Only Lp corrections were applied.

The structure was solved by direct methods using the *SHELXTL-Plus* (Siemens, 1990) programs. After non-H atoms were refined anisotropically, positions of all H atoms were calculated but were not refined further. The function minimized was $\sum w(F_o - F_c)^2$, where $w = 1/[\sigma^2(F_o) + 0.0003F_o^2]$. Four strong reflections with $(F_o - F_c)/\sigma > 4.0$ were excluded from the final refinement cycles, giving 1442 reflections with $F_o > 5\sigma(F)$. The final cycle of the full-matrix least-squares refinement gave $R = 0.091$, $wR = 0.087$ and $S = 2.56$ [$S = (n - m)^{-1} \sum_i (F_o^i - F_c^i)^2 / \sigma^2$, $n = 1442$, $m = 253$]. The high R value is due to the low quality of the crystal. For all parameters the final shift/ σ ratio was smaller than 0.061, the highest peak in the final

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
N(1)	7053 (6)	1831 (2)	2773 (6)	52 (2)
N(2)	5666 (5)	1600 (2)	2435 (5)	44 (2)
N(3)	4247 (6)	812 (2)	3025 (5)	42 (2)
C(1)	7851 (7)	1449 (3)	3688 (7)	52 (3)
C(2)	6990 (8)	998 (3)	3968 (6)	55 (3)
C(3)	5570 (7)	1109 (3)	3140 (6)	42 (3)
C(4)	3101 (7)	978 (2)	2034 (6)	41 (2)
C(5)	3216 (7)	1455 (3)	946 (7)	50 (3)
C(6)	4377 (7)	1901 (3)	1625 (7)	52 (3)
C(7)	1683 (7)	678 (3)	1938 (7)	44 (3)
C(8)	399 (8)	825 (3)	931 (8)	65 (3)
C(9)	-904 (8)	534 (4)	901 (9)	77 (4)
C(10)	-961 (9)	110 (4)	1863 (10)	75 (4)
C(11)	314 (10)	-36 (3)	2856 (9)	85 (4)
C(12)	1637 (8)	239 (3)	2905 (7)	62 (3)
C(13)	3579 (7)	1205 (3)	-488 (6)	48 (3)
C(14)	2849 (8)	1424 (3)	-1827 (7)	68 (3)
C(15)	3137 (9)	1215 (4)	-3121 (7)	74 (3)
C(16)	4133 (8)	781 (4)	-3080 (7)	65 (3)
C(17)	4886 (7)	568 (3)	-1755 (8)	54 (3)
C(18)	4614 (7)	780 (3)	-474 (6)	50 (3)
C(19)	3730 (7)	2310 (3)	2591 (7)	53 (3)
C(20)	2766 (9)	2731 (3)	1915 (7)	77 (3)
C(21)	2160 (9)	3103 (3)	2739 (10)	85 (4)
C(22)	2490 (10)	3059 (3)	4239 (10)	78 (4)
C(23)	3395 (10)	2639 (3)	4902 (8)	81 (4)
C(24)	4033 (9)	2267 (3)	4092 (7)	76 (3)
C(25)	9484 (8)	1541 (3)	4264 (9)	81 (4)

ΔF map was 0.34 e \AA^{-3} , the minimum -0.32 e \AA^{-3} . The final atomic parameters are listed in Table 1.* Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) were used.

Discussion. Fig. 1. shows a perspective view of molecule (I) with the atom-numbering scheme. Bond lengths, angles and selected torsion angles are listed in Table 2. The N(3)—C(4) and C(4)—C(5) bond lengths [1.294 (7) and 1.533 (9) Å] and the presence of an H atom at C(5) but not at N(3) suggest the imine tautomeric structure of (I) in contrast to dihydro[1,2,4]triazolo[2,3-*a*]pyrimidines, which crystallize as enamines (Orlov, Desenko *et al.*, 1988). The C(6)—C(19) and C(5)—C(13) bonds [1.532 (9) and 1.568 (9) Å] are somewhat longer than the standard value of 1.503 Å (Allen *et al.*, 1987). This may be due to repulsion between *ortho* H atoms of the phenyl substituents [H(18), H(20) and H(24)] and atoms of the dihydropyrimidine ring: the H(18)⋯C(3), H(20)⋯C(6) and H(24)⋯N(2) non-bonded distances [2.69 (1), 2.64 (1) and 2.54 (1) Å, respectively] are distinctly shorter than the sums of the corresponding van der Waals radii.

* 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 55849 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å), angles (°) and relevant torsion angles (°)

N(1)—N(2)	1.361 (7)	C(8)—C(9)	1.379 (11)
N(1)—C(1)	1.336 (8)	C(9)—C(10)	1.352 (13)
N(2)—C(3)	1.340 (8)	C(10)—C(11)	1.363 (11)
N(2)—C(6)	1.440 (7)	C(11)—C(12)	1.376 (12)
N(3)—C(3)	1.392 (8)	C(13)—C(14)	1.374 (9)
N(3)—C(4)	1.294 (7)	C(13)—C(18)	1.382 (9)
C(1)—C(2)	1.387 (10)	C(14)—C(15)	1.387 (11)
C(1)—C(25)	1.495 (9)	C(15)—C(16)	1.369 (12)
C(2)—C(3)	1.384 (8)	C(16)—C(17)	1.365 (9)
C(4)—C(5)	1.533 (9)	C(17)—C(18)	1.372 (10)
C(4)—C(7)	1.473 (9)	C(19)—C(20)	1.381 (10)
C(5)—C(6)	1.529 (8)	C(19)—C(24)	1.369 (9)
C(5)—C(13)	1.568 (9)	C(20)—C(21)	1.368 (12)
C(6)—C(19)	1.532 (9)	C(21)—C(22)	1.366 (13)
C(7)—C(8)	1.375 (8)	C(22)—C(23)	1.348 (11)
C(7)—C(12)	1.378 (10)	C(23)—C(24)	1.376 (12)
N(2)—N(1)—C(1)	103.3 (5)	C(8)—C(7)—C(12)	118.8 (6)
N(1)—N(2)—C(3)	113.4 (5)	C(7)—C(8)—C(9)	120.0 (7)
N(1)—N(2)—C(6)	123.0 (5)	C(8)—C(9)—C(10)	121.4 (7)
C(3)—N(2)—C(6)	122.7 (5)	C(9)—C(10)—C(11)	118.5 (8)
C(3)—N(3)—C(4)	117.5 (5)	C(10)—C(11)—C(12)	121.7 (8)
N(1)—C(1)—C(2)	112.3 (5)	C(7)—C(12)—C(11)	119.6 (6)
N(1)—C(1)—C(25)	119.6 (6)	C(5)—C(13)—C(14)	118.7 (6)
C(2)—C(1)—C(25)	128.2 (6)	C(5)—C(13)—C(18)	123.2 (5)
C(1)—C(2)—C(3)	105.1 (6)	C(14)—C(13)—C(18)	118.1 (6)
N(2)—C(3)—N(3)	123.5 (5)	C(13)—C(14)—C(15)	120.5 (7)
N(2)—C(3)—C(2)	105.9 (6)	C(14)—C(15)—C(16)	120.3 (6)
N(3)—C(3)—C(2)	130.6 (6)	C(15)—C(16)—C(17)	119.7 (7)
N(3)—C(4)—C(5)	121.6 (6)	C(16)—C(17)—C(18)	119.9 (6)
N(3)—C(4)—C(7)	117.9 (5)	C(13)—C(18)—C(17)	121.5 (5)
C(5)—C(4)—C(7)	120.5 (5)	C(6)—C(19)—C(20)	118.6 (6)
C(4)—C(5)—C(6)	112.1 (5)	C(6)—C(19)—C(24)	122.8 (6)
C(4)—C(5)—C(13)	110.8 (5)	C(20)—C(19)—C(24)	118.5 (7)
C(6)—C(5)—C(13)	110.0 (5)	C(19)—C(20)—C(21)	120.4 (7)
N(2)—C(6)—C(5)	107.2 (5)	C(20)—C(21)—C(22)	120.4 (7)
N(2)—C(6)—C(19)	112.9 (5)	C(21)—C(22)—C(23)	119.5 (8)
C(5)—C(6)—C(19)	110.0 (5)	C(22)—C(23)—C(24)	120.9 (7)
C(4)—C(7)—C(8)	122.4 (6)	C(19)—C(24)—C(23)	120.3 (7)
C(4)—C(7)—C(12)	118.8 (5)		
C(1)—N(1)—N(2)—C(3)	2.4 (4)	N(3)—C(4)—C(7)—C(12)	0.3 (5)
N(1)—N(2)—C(3)—C(2)	-1.8 (5)	N(3)—C(4)—C(5)—C(6)	-32.6 (4)
N(2)—C(3)—C(2)—C(1)	0.4 (5)	N(3)—C(4)—C(5)—C(13)	90.7 (4)
C(3)—C(2)—C(1)—N(1)	1.2 (5)	C(4)—C(5)—C(6)—N(2)	43.5 (5)
C(2)—C(1)—N(1)—N(2)	-2.2 (4)	C(4)—C(5)—C(6)—C(19)	-79.5 (5)
N(1)—N(2)—C(3)—N(3)	176.5 (3)	C(5)—C(6)—N(2)—C(3)	-34.1 (5)
N(2)—C(3)—N(3)—C(4)	9.7 (4)	C(4)—C(5)—C(13)—C(18)	-42.7 (4)
C(3)—N(3)—C(4)—C(5)	4.6 (5)	C(5)—C(6)—C(19)—C(20)	-77.5 (5)
C(3)—N(3)—C(4)—C(7)	-178.0 (5)		

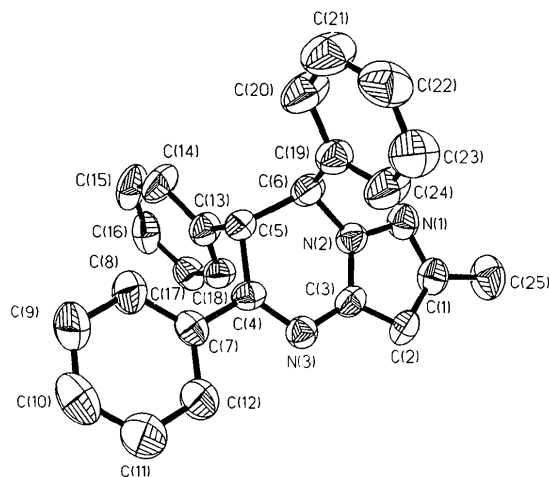


Fig. 1. A view of the title molecule with the atom-numbering scheme. Atoms are presented as 50% probability ellipsoids.

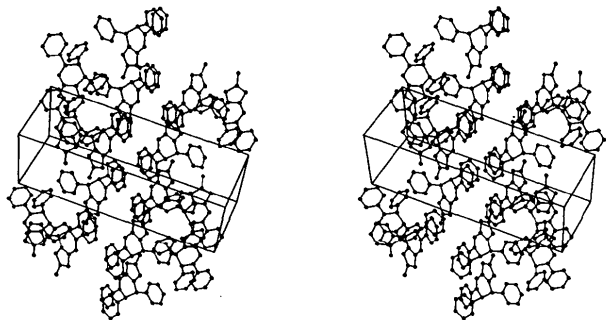


Fig. 2. A stereoscopic view of the packing for compound (I).

The torsion angles indicate that the pyrazole ring in (I) is planar. The conformation of the dihydropyrimidine ring can be described as a distorted sofa with the C(5) atom displaced most from the plane of the ring [puckering coordinates (Zefirov, Palyulin & Dashevskaya, 1990) are: $S = 0.56$, $\varphi = 27.4^\circ$, $\theta = 45.4^\circ$]. The *trans* substituents at C(5) and C(6) have an axial orientation. The N(3)—C(4)—C(7)—C(12) and N(2)—C(3)—N(3)—C(4) torsion angles are

$0.3(3)$ and $9.7(5)^\circ$, respectively, indicating conjugation of the π systems of the C(7)—C(8)—C(9)—C(10)—C(11)—C(12) aromatic ring, azomethyne group and pyrazole ring.

A stereoscopic view of the unit cell is shown in Fig. 2. There are no intermolecular distances shorter than the sums of the van der Waals radii.

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