

studies is 0.011 Å, with the largest difference at C(5)–C(6) where MMPI predicts a bond length longer by 0.023 Å. Similarly, the r.m.s. difference in internal bond angles is 0.9°, with the largest difference at C(5)–C(14)–C(13), where MMPI predicts a bond angle larger by 2.6°. Equally good agreement is found with the torsion angles.

Possible systematic differences in the relative magnitudes of the carbon-atom bond distances and endocyclic angles [$p(i)$] for the fused-ring system derived by the two methods were examined by comparing $\langle [p(i)_{X\text{-ray}} - p(i)_{\text{MMPI}}] \rangle$ with $\langle \sigma p(i) \rangle$. Neither the bond angles nor the 'single'-bond lengths (defined arbitrarily as > 1.40 Å) displayed any systematic variation on this basis. However, there was some indication that the 'double'-bond lengths calculated by MMPI were systematically larger than those obtained from the X-ray data $\{ \langle [p(i)_{X\text{-ray}} - p(i)_{\text{MMPI}}] \rangle = -0.015 \text{ \AA} \}$.

Finally, MMPI predicts orientation of the phenyl groups to each other, and to ring *B* which, within experimental error, are indistinguishable from the crystallographic results.

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Structure of 2-[Hydroxy(methoxycarbonyl)methyl]-2-methoxycarbonyl-4,6-dimethyl-1-phenyl-1,2-dihydropyrimidinium Picrate, $C_{17}H_{21}N_2O_5^+ \cdot C_6H_2N_3O_7^-$

BY E. GUTIÉRREZ-PUEBLA, A. MONGE, C. RUIZ-VALERO* AND A. RODRÍGUEZ-ROLDÁN

Instituto de Química Inorgánica 'Elhúyar', Serrano 113, 28006 Madrid, Spain

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Abstract. $M_r = 561.5$, triclinic, $P\bar{1}$, $a = 8.113$ (3), $b = 12.289$ (2), $c = 13.523$ (3) Å, $\alpha = 97.20$ (2), $\beta = 105.67$ (2), $\gamma = 89.11$ (2)°, $V = 1287.7$ Å³, $Z = 2$, $D_x = 1.45$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.114$ cm⁻¹, $F(000) = 584$, $T = 290$ K, $R = 0.051$ for 2161 observed reflexions. The structure of the title compound has been established, thus confirming the occurrence of ring expansion in its synthesis by reaction of 1-[1,2-bis(methoxycarbonyl)-1-vinyl]-3,5-dimethyl-2-phenylpyrazolium tetrafluoroborate with alkali. Bond lengths and angles are normal. Two asymmetrically bifurcated hydrogen bonds link the anion to the cation.

Introduction. By reaction of 1-[1,2-bis(methoxycarbonyl)-1-vinyl]-3,5-dimethyl-2-phenylpyrazolium tetrafluoroborate with alkali, a mixture of two

diastereoisomeric dihydropyrimidines is obtained: (*RR,SS*) and (*RS,SR*)-2-[hydroxy(methoxycarbonyl)-methyl]-2-methoxycarbonyl-4,6-dimethyl-1-phenyl-1,2-dihydropyrimidine. Afterwards, this mixture was treated with acid and it was observed through ¹H NMR spectroscopy that only one of the two possible diastereoisomeric salts was formed (Elguero, de la Hoz & Pardo, 1984).

We have determined the crystal structure of the title compound in order to establish the molecular structure of the compound and thus the nature of the expansion in the pyrazole ring, and also to establish the stereochemistry of the salt obtained as a product of the reaction with acid.

Experimental. Clear colourless, prismatic crystal 0.5 × 0.2 × 0.3 mm. Enraf–Nonius CAD-4F automatic diffractometer, cell dimensions refined by least-squares fitting of θ values of 25 reflexions; intensities of 5591 unique reflexions, $1 < \theta < 27^\circ$, *hkl*

* Author for correspondence. Departamento de Química Inorgánica, Facultad de Químicas, Universidad Complutense, 28003 Madrid, Spain.

−10,−15,0 to 10,15,17, monochromatic Mo *K*α radiation, $\omega/2\theta$ scans; three reflexions monitored periodically during data collection showed no crystal decomposition; intensities corrected for Lorentz and polarization effects; 2161 considered observed [$I > 2\sigma(I)$]; no absorption correction; scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974). Structure solved with *MULTAN77* (Main, Lessinger, Woolfson, Germain &

Declercq, 1977), best *E* map revealed all non-H atoms; anisotropic full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized, $R = 0.068$; difference

Table 1. Atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \cos(a_i, a_j).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
N(1)	0.6484 (5)	0.3303 (3)	0.1775 (3)	35 (1)
N(2)	0.8533 (5)	0.3198 (3)	0.3383 (3)	38 (1)
C(1)	0.8331 (6)	0.3247 (4)	0.2275 (3)	35 (2)
C(2)	0.7658 (7)	0.3886 (4)	0.3868 (4)	41 (2)
C(3)	0.6285 (7)	0.4419 (4)	0.3287 (4)	43 (2)
C(4)	0.5609 (6)	0.4008 (4)	0.2260 (4)	41 (2)
C(5)	0.9308 (6)	0.4307 (4)	0.2217 (4)	40 (2)
O(51)	0.8407 (4)	0.4924 (3)	0.1531 (3)	49 (1)
O(52)	1.0720 (4)	0.4506 (3)	0.2756 (3)	53 (1)
C(6)	0.9311 (10)	0.5897 (5)	0.1418 (6)	71 (3)
C(7)	0.9222 (6)	0.2206 (4)	0.1881 (4)	38 (2)
O(71)	0.8388 (5)	0.1250 (3)	0.2000 (3)	53 (1)
C(8)	0.9347 (6)	0.2238 (4)	0.0789 (4)	42 (2)
O(81)	0.8971 (5)	0.1280 (3)	0.0207 (3)	53 (1)
O(82)	0.9872 (5)	0.3039 (3)	0.0525 (3)	58 (2)
C(9)	0.9162 (8)	0.1243 (5)	−0.0839 (4)	68 (3)
C(10)	0.8057 (8)	0.4003 (4)	0.5017 (4)	57 (2)
C(11)	0.3840 (7)	0.4301 (5)	0.1696 (5)	61 (2)
C(12)	0.5698 (6)	0.2729 (4)	0.0749 (3)	36 (2)
C(13)	0.4807 (7)	0.1752 (4)	0.0671 (4)	50 (2)
C(14)	0.3971 (7)	0.1237 (4)	−0.0309 (5)	62 (2)
C(15)	0.4052 (7)	0.1691 (6)	−0.1179 (4)	66 (3)
C(16)	0.4926 (8)	0.2652 (6)	−0.1082 (4)	71 (3)
C(17)	0.5754 (7)	0.3184 (4)	−0.0118 (4)	52 (2)
C(18)	0.1679 (6)	0.0879 (4)	0.4553 (4)	41 (2)
O(18)	0.0625 (5)	0.1391 (3)	0.3945 (3)	57 (1)
C(19)	0.3050 (6)	0.1392 (4)	0.5417 (4)	44 (2)
N(19)	0.3274 (6)	0.2580 (3)	0.5554 (4)	62 (2)
O(191)	0.4689 (6)	0.2962 (3)	0.6034 (4)	100 (2)
O(192)	0.2110 (6)	0.3151 (3)	0.5193 (4)	118 (3)
C(20)	0.4194 (6)	0.0832 (4)	0.6100 (4)	43 (2)
C(21)	0.4085 (6)	−0.0299 (4)	0.5983 (4)	41 (2)
N(21)	0.5291 (6)	−0.0908 (4)	0.6705 (3)	52 (2)
O(211)	0.6366 (5)	−0.0384 (3)	0.7415 (3)	78 (2)
O(212)	0.5211 (5)	−0.1910 (3)	0.6571 (3)	73 (2)
C(22)	0.2897 (6)	−0.0876 (4)	0.5164 (4)	42 (2)
C(23)	0.1764 (6)	−0.0306 (4)	0.4483 (3)	39 (2)
N(23)	0.0599 (6)	−0.0973 (4)	0.3613 (3)	55 (2)
O(231)	0.0936 (9)	−0.1906 (4)	0.3422 (4)	163 (3)
O(232)	−0.0619 (6)	−0.0595 (3)	0.3088 (4)	88 (2)

Table 2. Bond lengths (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

N(1)–C(1)	1.473 (6)	C(13)–C(14)	1.391 (7)
N(1)–C(4)	1.332 (6)	C(14)–C(15)	1.381 (10)
N(1)–C(12)	1.456 (5)	C(15)–C(16)	1.361 (10)
N(2)–C(1)	1.472 (6)	C(16)–C(17)	1.380 (7)
N(2)–C(2)	1.320 (7)	C(18)–O(18)	1.240 (6)
C(1)–C(5)	1.557 (7)	C(18)–C(19)	1.461 (6)
C(1)–C(7)	1.566 (7)	C(18)–C(23)	1.449 (7)
C(2)–C(3)	1.386 (7)	C(19)–N(19)	1.456 (6)
C(2)–C(10)	1.488 (7)	C(19)–C(20)	1.366 (7)
C(3)–C(4)	1.381 (7)	N(19)–O(191)	1.224 (6)
C(4)–C(11)	1.494 (7)	N(19)–O(192)	1.200 (6)
C(5)–O(51)	1.328 (6)	C(20)–C(21)	1.381 (7)
C(5)–O(52)	1.190 (6)	C(21)–N(21)	1.454 (6)
C(6)–O(51)	1.458 (8)	C(21)–C(22)	1.381 (6)
C(7)–O(71)	1.412 (6)	N(21)–O(211)	1.228 (5)
C(7)–C(8)	1.513 (7)	N(21)–O(212)	1.222 (6)
C(8)–O(81)	1.322 (6)	C(22)–C(23)	1.367 (6)
C(8)–O(82)	1.209 (7)	C(23)–N(23)	1.460 (6)
C(9)–O(81)	1.459 (7)	N(23)–O(231)	1.188 (7)
C(12)–C(13)	1.389 (7)	N(23)–O(232)	1.177 (6)
C(12)–C(17)	1.372 (8)		
C(4)–N(1)–C(12)	121.5 (4)	C(13)–C(12)–C(17)	121.1 (5)
C(1)–N(1)–C(12)	122.0 (4)	C(12)–C(13)–C(14)	118.6 (5)
C(1)–N(1)–C(4)	116.1 (4)	C(13)–C(14)–C(15)	120.1 (6)
C(1)–N(2)–C(2)	118.4 (4)	C(14)–C(15)–C(16)	120.2 (5)
N(1)–C(1)–N(2)	107.3 (4)	C(15)–C(16)–C(17)	120.8 (6)
N(2)–C(1)–C(7)	106.1 (4)	C(12)–C(17)–C(16)	119.2 (5)
N(2)–C(1)–C(5)	105.9 (4)	C(19)–C(18)–C(23)	110.7 (4)
N(1)–C(1)–C(7)	114.8 (4)	O(18)–C(18)–C(23)	124.9 (5)
N(1)–C(1)–C(5)	111.8 (4)	O(18)–C(18)–C(19)	124.4 (5)
C(5)–C(1)–C(7)	110.4 (4)	C(18)–C(19)–C(20)	124.6 (5)
N(2)–C(2)–C(10)	119.9 (5)	C(18)–C(19)–N(19)	118.8 (4)
N(2)–C(2)–C(3)	118.9 (5)	N(19)–C(19)–C(20)	116.6 (4)
C(3)–C(2)–C(10)	121.1 (5)	C(19)–N(19)–O(192)	120.5 (5)
C(2)–C(3)–C(4)	118.2 (5)	C(19)–N(19)–O(191)	117.5 (4)
N(1)–C(4)–C(3)	120.7 (5)	O(191)–N(19)–O(192)	122.0 (5)
C(3)–C(4)–C(11)	120.1 (5)	C(19)–C(20)–C(21)	119.2 (5)
N(1)–C(4)–C(11)	119.1 (5)	C(20)–C(21)–C(22)	121.4 (5)
C(1)–C(5)–O(51)	113.3 (4)	C(20)–C(21)–N(21)	119.9 (4)
C(1)–C(5)–O(52)	120.7 (4)	N(21)–C(21)–C(22)	118.7 (4)
O(51)–C(5)–O(52)	125.9 (5)	C(21)–N(21)–O(212)	119.0 (4)
C(5)–O(51)–C(6)	114.9 (5)	C(21)–N(21)–O(211)	117.9 (5)
C(1)–C(7)–C(8)	111.7 (4)	O(211)–N(21)–O(212)	123.1 (5)
C(1)–C(7)–O(71)	109.7 (4)	C(21)–C(22)–C(23)	118.8 (5)
O(71)–C(7)–C(8)	113.4 (4)	C(18)–C(23)–C(22)	125.2 (4)
C(7)–C(8)–O(82)	122.2 (4)	C(22)–C(23)–N(23)	115.6 (4)
C(7)–C(8)–O(81)	112.6 (4)	C(18)–C(23)–N(23)	119.3 (4)
O(81)–C(8)–O(82)	124.9 (5)	O(23)–N(23)–O(232)	121.4 (5)
C(8)–O(81)–C(9)	115.2 (4)	C(23)–N(23)–O(231)	118.4 (5)
N(1)–C(12)–C(17)	120.2 (4)	O(231)–N(23)–O(232)	120.2 (5)
N(1)–C(12)–C(13)	118.6 (4)		

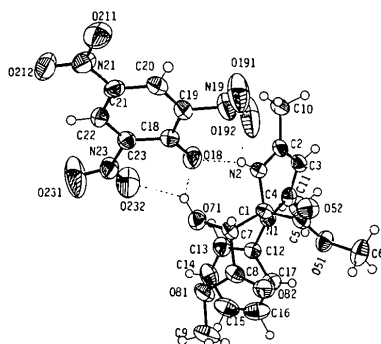


Fig. 1. ORTEP (Johnson, 1965) drawing of the cation and anion showing the atom numbering.

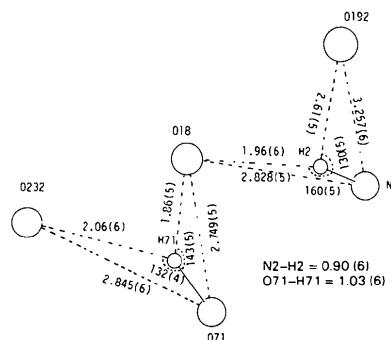


Fig. 2. Schematic drawing showing the geometrical features of the hydrogen-bond network (lengths in \AA , angles in degrees). Atoms of the anion are at $1+x, y, z$.

synthesis calculated with reflexions having $\sin\theta/\lambda < 0.5 \text{ \AA}^{-1}$ showed all H atoms as highest peaks of the map; final refinement with fixed isotropic temperature factors for H atoms and unit weights led to $R = 0.051$; max. and average shift/error in final LS cycle 2.68 and 0.21 (including H atoms); final difference synthesis had no electron density > 0.31 and $< -0.28 \text{ e \AA}^{-3}$. No correction for secondary extinction. Most of the calculations performed with *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. Table 1* contains the final atomic parameters; Fig. 1 (Johnson, 1965) shows the geometry of the structure and the atom labelling. Bond lengths and angles together with their e.s.d.'s are in Table 2.

Two asymmetrically bifurcated hydrogen bonds of the type reported by Monge, Martínez-Ripoll & García-Blanco (1978) have been located. The geometrical features of the hydrogen-bond network, calculated with *PARST5* (Nardelli, Musatti, Domiano & Andreotti, 1965), are shown in Fig. 2.

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39832 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

As was expected, the initial pyrazole ring has experienced an expansion in the course of the reaction leading to a dihydropyrimidine derivative.

Through the crystal-structure determination it has been established that of the two diastereoisomers, (*RR,SS*) and (*RS,SR*), that isolated as the salt was the (*RS,SR*).

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Structure of Diethyl 1,4-Dihydro-2,4,6-trimethyl-3,5-pyridinedicarboxylate, $\text{C}_{14}\text{H}_{21}\text{NO}_4$

BY S. FORTIER, M. E. FRASER, N. J. MOORE, Y. S. PARK AND R. A. WHITNEY

Department of Chemistry, Queen's University, Kingston, Canada K7L 3N6

AND G. S. MARKS

Department of Pharmacology and Toxicology, Queen's University, Kingston, Canada K7L 3N6

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Abstract. $M_r = 267.3$, monoclinic, $P2_1/a$, $a = 16.921$ (3), $b = 7.483$ (2), $c = 11.429$ (2) Å, $\beta = 94.24$ (2)°, $V = 1443.2 \text{ \AA}^3$, $Z = 4$, $D_x = 1.230 \text{ g cm}^{-3}$, $\lambda(\text{Cu } K\alpha) = 1.54184 \text{ \AA}$, $\mu = 7.01 \text{ cm}^{-1}$, $F(000) = 576$, $T = 293 \text{ K}$, final $R = 0.056$ for 1371 observed reflections. The dihydropyridine ring adopts a flat-boat conformation. The C(4) methyl substituent is approximately perpendicular to the dihydropyridine ring. The two ethoxycarbonyl groups are twisted in opposite directions so that the molecule does not have mirror symmetry.

Introduction. In recent years 1,4-dihydro-3,5-pyridinedicarboxylates have become of great interest due to their biological activity. The 4-aryl derivatives represent a new class of highly active calcium antagonists (Bossert, Meyer & Wehinger, 1981) while the 4-alkyl derivatives exhibit porphyrinogenic activity in a variety of animals (Marks, 1978). In this latter case the nature of the biological activity observed is dependent on the structure of the 4-alkyl group (Augusto, Beilan & Ortiz de Montellano, 1982). Since it is known that 1,4-dihydro-3,5-pyridinedicarboxylates can adopt a ring