

Structure of 3-Ethoxycarbonyl-1,2-dimethyl-4-pyrrolecarbaldehyde

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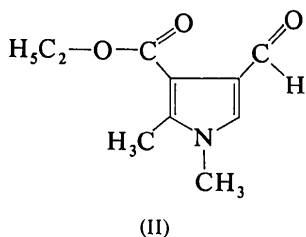
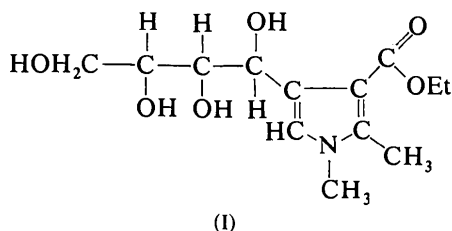
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Abstract. $C_{10}H_{13}NO_3$, $M_r = 195$, triclinic, $P\bar{1}$, $a = 9.378$ (6), $b = 8.543$ (5), $c = 7.603$ (4) Å, $\alpha = 116.91$ (4), $\beta = 108.93$ (4), $\gamma = 93.03$ (5)°, $V = 499.24$ Å³, $Z = 2$, $D_x = 1.30$ Mg m⁻³. The structure was solved by direct methods (*MULTAN*) with Mo radiation and X-ray diffractometer intensities and refined to $R = 0.049$ for 1191 observed reflexions [$I > 2.5\sigma(I)$]. Considerable delocalization of the double-bond π electrons is indicated by the bond lengths in the pyrrole ring.

Introduction. The title compound (II) was synthesized by degradative oxidation with sodium metaperiodate of the polyhydroxyalkylpyrrole (I) obtained by reaction of 1-methylamino-1-deoxy-D-arabinohexulose with ethyl acetoacetate (García-González, Fernández-Bolaños, Martín-Jimenez & Rovina, 1978). The present X-ray results confirm the structure derived by chemical and spectroscopic methods. Colourless crystals suitable for X-ray analysis were kindly supplied by Professor J. Fernández-Bolaños of the Departamento de Química



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Orgánica, Universidad de Sevilla. Rotation and Weissenberg photographs indicated triclinic symmetry and lattice parameters were obtained from diffractometric measurements. Intensities were collected on a Syntex diffractometer with Mo radiation. 1483 independent reflexions with $2\theta < 47^\circ$ were collected; of these, 1191 which had $I > 2.5\sigma(I)$ were considered as observed. Intensity data were corrected for Lorentz-polarization but not for absorption or extinction.

The crystal structure was solved by direct methods using *MULTAN* 78 (Main, Hull, Lessinger, Woolfson, Germain & Declercq, 1978). An *E* Fourier synthesis revealed the heavy atoms. All the H atoms were located

Table 1. Positional parameters ($\times 10^4$, for H $\times 10^3$) with their estimated standard deviations in parentheses

	x	y	z
N(1)	6876 (3)	11493 (3)	13506 (3)
C(2)	5319 (3)	10720 (4)	12750 (4)
C(3)	5227 (3)	9015 (4)	12531 (4)
C(4)	6779 (3)	8776 (4)	13182 (4)
C(5)	7742 (3)	10346 (4)	13761 (4)
C(6)	7511 (4)	13315 (4)	14013 (6)
C(7)	4139 (4)	11742 (5)	12410 (6)
C(8)	3836 (3)	7687 (4)	11874 (4)
O(9)	3849 (2)	6319 (3)	11989 (4)
O(10)	2526 (2)	8132 (3)	11114 (3)
C(11)	1084 (3)	6880 (5)	10437 (6)
C(12)	-207 (4)	7672 (6)	9814 (7)
C(13)	7301 (4)	7220 (4)	13202 (5)
O(14)	8647 (3)	7176 (3)	13939 (4)
H(5)	887 (4)	1072 (4)	1432 (4)
H(6A)	724 (3)	1422 (4)	1514 (4)
H(6B)	859 (4)	1353 (4)	1447 (4)
H(6C)	708 (3)	1345 (4)	1286 (5)
H(7A)	314 (4)	1123 (4)	1212 (4)
H(7B)	435 (3)	1290 (4)	1370 (4)
H(7C)	412 (3)	1209 (4)	1150 (5)
H(11A)	106 (3)	566 (4)	919 (4)
H(11B)	112 (3)	673 (4)	1155 (4)
H(12A)	-114 (4)	699 (4)	932 (4)
H(12B)	-3 (3)	897 (4)	1108 (4)
H(12C)	-17 (3)	788 (4)	877 (5)
H(13)	653 (3)	617 (4)	1255 (4)

Table 2. *Torsion angles* ($^{\circ}$)Standard deviations are 0.4 $^{\circ}$.

C(5)–N(1)–C(2)–C(3)	0.0	C(7)–C(2)–C(3)–C(4)	–177.5	C(3)–C(4)–C(5)–N(1)	0.0
C(5)–N(1)–C(2)–C(7)	177.9	C(7)–C(2)–C(3)–C(8)	0.0	C(13)–C(4)–C(5)–N(1)	178.5
C(6)–N(1)–C(2)–C(3)	–178.6	C(2)–C(3)–C(4)–C(5)	0.0	C(3)–C(4)–C(13)–O(14)	–173.8
C(6)–N(1)–C(2)–C(7)	0.0	C(2)–C(3)–C(4)–C(13)	–178.4	C(5)–C(4)–C(13)–O(14)	8.2
C(2)–N(1)–C(5)–C(4)	0.0	C(8)–C(3)–C(4)–C(5)	–177.2	C(3)–C(8)–O(10)–C(11)	180.0
C(6)–N(1)–C(5)–C(4)	178.5	C(8)–C(3)–C(4)–C(13)	4.5	O(9)–C(8)–O(10)–C(11)	0.0
N(1)–C(2)–C(3)–C(4)	0.0	C(2)–C(3)–C(8)–O(9)	6.9	C(8)–O(10)–C(11)–C(12)	175.8
N(1)–C(2)–C(3)–C(8)	177.0	C(4)–C(3)–C(8)–O(10)	–172.8		

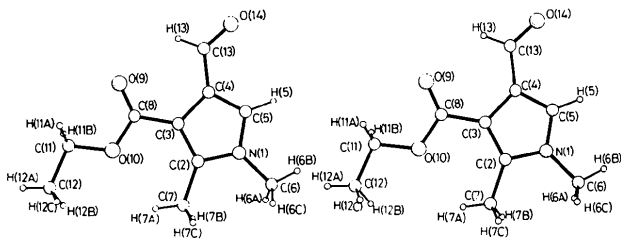


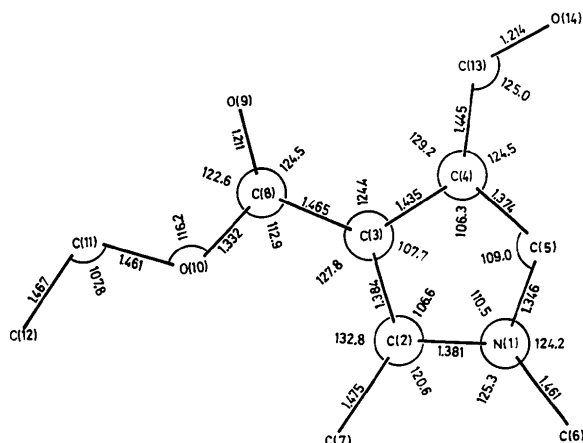
Fig. 1. A stereodrawing of the molecule.

on a difference Fourier map. The positional and thermal parameters were refined by a full-matrix least-squares method. The programs *SHELX 76* (Sheldrick, 1976) and *PLUTO 78* (Motherwell & Clegg, 1978) were used. Refinement with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors (not refined) for H atoms gave a discrepancy index $R = 0.049$. Final positional parameters are given in Table 1.*

Discussion. A stereoscopic drawing of the molecule, showing the atom-numbering scheme, is in Fig. 1. Bond lengths and angles (involving non-hydrogen atoms only) are presented in Fig. 2. The internal dimensions of the molecule are, in general, normal but present some points of interest. The lengthening of the formal double bonds C(2)–C(3) and C(4)–C(5) and the shortening of the other three bonds of the pyrrole ring indicate considerable delocalization of the double-bond π electrons. N(1)–C(5) is much shorter than N(1)–C(2) and this difference may be explained in terms of contributions from mesomeric forms (Sheldrick & Becker, 1978).

As expected, the pyrrole ring is planar. No deviations from the calculated plane exist for the five ring

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34390 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 2. Bond lengths (\AA) and angles ($^{\circ}$) involving the non-hydrogen atoms (standard deviations are 0.004 \AA and 0.2 $^{\circ}$ respectively).

atoms. The near planarity of the molecule is illustrated by the torsion angles between the bond segments listed in Table 2.

The packing of the molecules in the crystal is determined by van der Waals interactions only. No evidence for hydrogen bonds exists and there are no intermolecular contacts shorter than the respective van der Waals diameters.

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