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Ethyl 2-(Methylaminomethylene)-3-(2-methyl-6-oxopiperidino)-3-oxopropionate

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Abstract. $C_{13}H_{20}N_2O_4$, $M_r = 268 \cdot 17$, monoclinic, $P2_1/c$, $a = 10 \cdot 322$ (3), $b = 17 \cdot 218$ (6), $c = 8 \cdot 698$ (3) Å, $\beta = 112 \cdot 25$ (3)°, $Z = 4$, $V = 1430 \cdot 72$ Å³, $D_c = 0 \cdot 750$ Mg m⁻³, μ(Cu $K\alpha$) = $0 \cdot 68$ mm⁻¹. $R = 0 \cdot 058$ for 1949 observed reflections. The geometry of the piperidine ring can be approximated to a flattened half-chair. The conformation of the ethyl 2-(methylaminomethylene)-3-oxopropionate side chain is stabilized by an intramolecular hydrogen bond. The crystal structure is held together by intermolecular hydrogen bonds besides the van der Waals forces.

Introduction. Among the homopyrimidazole derivatives, 3-ethoxycarbonyl-1,6-dimethyl-4-oxo-3,4,6,7,8,9-hexahydro-2*H*-pyrido[1,2-*a*]pyrimidinium methane-

sulphonate, Probon^R (Negwer, 1971), was found to be a new analgesic drug. However, it is believed that this drug must undergo biological metabolism to form the immediately active molecule (Simon, Mészáros & Sasvári, 1975). In the course of studies concerning the metabolism of Probon^R, the title compound (4 in Fig. 1) was isolated from alkaline solution (Mészáros, 1978). Because its structure could not be completely derived by spectroscopic methods, an X-ray structure analysis was undertaken.

The unit-cell dimensions were refined by least-squares fitting of the cell parameters to a powder pattern, taken in a Guinier–Hägg-type focusing camera with Cu $K\alpha_1$ ($\lambda = 1 \cdot 5405$ Å) radiation and KCl ($a = 6 \cdot 2930$ Å at 298 K) as internal standard. The intensity
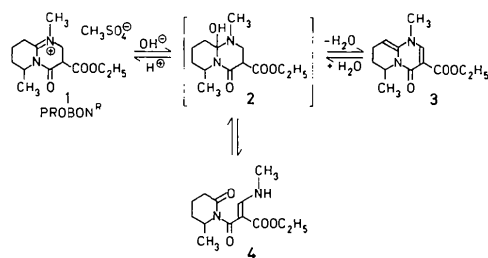
Fig. 1. Schematic figure showing the hydrolysis of Probon[R] in alkaline solution.

data were collected on a computer-controlled PW 1100 diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. 2553 unique reflections were measured ($\theta \leq 65°$) and corrected for Lorentz and polarization effects.

The structure was solved by the *MULTAN* 74 program system (Main, Lessinger, Woolfson, Germain & Declercq, 1974). 250 E values ($E_{min} = 1\cdot64$) and 2000 triple relations among them were used to generate eight trial phase sets. The E map calculated from the best solution gave the approximate positions of 18 non-H atoms. The model was completed by conventional difference Fourier syntheses and refined by the full-matrix least-squares method, using the *SHELX* 76 program system (Sheldrick, 1976). The positions of the 19 non-H atoms were refined together with their anisotropic thermal parameters. Each H atom was given the same isotropic temperature factor as the non-H atom to which it is linked. The methyl groups were treated as rigid groups (C—H = $1\cdot08$ Å), but individual positional parameters were refined for the remaining H atoms. The final agreement factors were $R = 0\cdot058$ and $R_w = 0\cdot067$ for 1949 structure factors, all with $F \geq 6\sigma(F)$. The weights used were calculated as $w = k/\sigma^2(F) + |g|.F^2$ (Sheldrick, 1976), with g refined to the value of $0\cdot0012$. The atomic scattering factors for the non-H atoms were taken from Cromer & Mann (1968) and Cromer & Liberman (1970) and, for the H atoms, from Stewart, Davidson & Simpson (1965). The final atomic coordinates of the non-H atoms are listed in Table 1.* The atomic labelling used is shown in Fig. 2.

Discussion. The NMR spectra indicate that in solution the title compound (Fig. 3) exists in two isomeric forms, where the positions of the enamine N(13) atom

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* Lists of structure factors, anisotropic thermal parameters of the non-H atoms, coordinates of the H atoms and the equations of the least-squares planes and deviations of the atoms from the planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38063 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *for the non-*H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	U_{eq}
N(1)	1987 (2)	9775 (1)	6822 (3)	46 (1)
C(2)	1601 (2)	9229 (1)	5558 (3)	45 (1)
C(3)	1970 (3)	9371 (2)	4055 (4)	61 (2)
C(4)	2828 (4)	10072 (2)	4086 (5)	74 (2)
C(5)	2336 (4)	10733 (2)	4848 (5)	71 (2)
C(6)	2547 (3)	10564 (2)	6667 (4)	60 (2)
O(7)	933 (2)	8652 (1)	5591 (2)	56 (1)
C(8)	4041 (4)	10632 (2)	7866 (5)	97 (2)
C(9)	1736 (3)	9649 (1)	8320 (3)	49 (1)
O(10)	1459 (3)	10214 (1)	8986 (3)	71 (1)
C(11)	1811 (3)	8866 (1)	8982 (3)	47 (1)
C(12)	863 (3)	8709 (1)	9729 (3)	47 (1)
N(13)	649 (2)	8047 (1)	10334 (3)	50 (1)
C(14)	−427 (3)	7926 (2)	11011 (4)	61 (2)
C(15)	2766 (3)	8264 (1)	8896 (3)	46 (1)
O(16)	2740 (2)	7593 (1)	9333 (3)	64 (1)
O(17)	3773 (2)	8514 (1)	8378 (2)	53 (1)
C(18)	4757 (3)	7935 (2)	8296 (5)	61 (2)
C(19)	5715 (3)	8314 (2)	7599 (5)	81 (2)

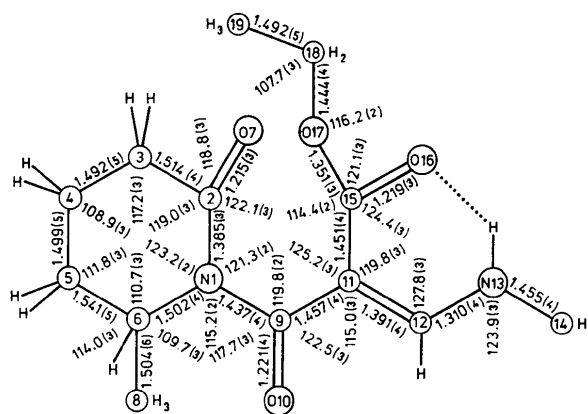
Fig. 2. Interatomic distances (Å) and bond angles (°) involving the non-H atoms of the molecule, with atoms numbered as in the text. (The e.s.d.'s are given in parentheses.)

and the carboxyl group relative to the C(11)=C(12) double bond are different (Pusztay, 1979; Simon, 1980). The X-ray analysis revealed that in the solid state only the Z (= *zusammen*) isomer is present.

Four of the piperidine ring atoms are coplanar within $0\cdot09$ Å (plane 1), while the remaining two atoms, C(4) and C(5), are located on either side of this plane indicating a half-chair conformation. This conclusion was checked by geometrical calculations. The fact that only one asymmetry parameter [according to Duax, Weeks & Rohrer (1976)] assumes a low value [$\Delta C_2 = 8\cdot3°$], and also the specific set of puckering
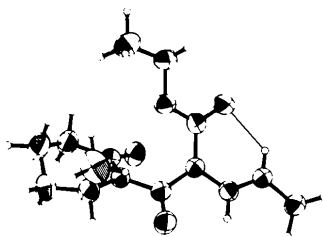
$C_{13}H_{20}N_2O_4$

Fig. 3. View of the title molecule. The non-H atoms are represented by their thermal ellipsoids corresponding to 50% probability. The H atoms are drawn as spheres with constant radius.
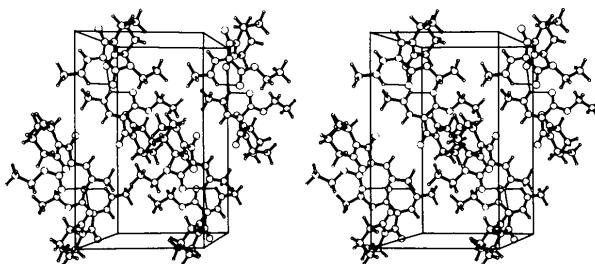

Fig. 4. Stereoscopic packing diagram of the crystal structure (y is vertical, x is to the right and z is out of the paper).

parameters obtained [according to Cremer & Pople (1975)] [$\varphi = 321\cdot4$, $\theta = 121\cdot6°$ and $Q = 0\cdot514$ Å], point to a near half-chair conformation, with an approximate twofold rotation axis through the N(1)—C(2) and C(4)—C(5) bonds.

The ring N atom is only displaced $0\cdot046$ Å from the plane defined by the three C atoms to which it is bonded: C(2), C(6) and C(9). The sum of the angles around N(1) is $359\cdot7°$, showing the central atom to be sp^2-hybridized. Two of the three N(1)—C single bonds are conjugated, but have different degrees of double-bond contribution.

In the ethyl 2-(methylaminomethylene)-3-oxo-propionate side chain, atoms C(11), C(12), N(13), C(15) and O(16) are coplanar within $0\cdot05$ Å (plane 2), and atom O(16) is attached by an intramolecular hydrogen bond to atom N(13) [N$\cdots$O $= 2\cdot730$ (3), N—H $= 0\cdot93$ (3), H$\cdots$O $= 2\cdot09$ (3) Å and $\angle$N—H$\cdots$O $= 125$ (3)°]. The enamine N atom is sp^2-hybridized [sum of the angles around N(13) is $360°$]. The angle between the normals to plane (1) and plane (2) is 53 (3)°.

The packing of the molecules is illustrated in Fig. 4. The carbonyl O(7) of the piperidine ring is the acceptor in an intermolecular hydrogen bond from the N(13) amine atom [N$\cdots$O $= 2\cdot940$ (3), N—H $= 0\cdot93$ (3), H$\cdots$O $= 2\cdot20$ (3) Å and $\angle$N—H$\cdots$O $= 135$ (3)°]. Accordingly, H(13) is a bifurcated H atom [$\angle$O(7)$\cdots$H(13)$\cdots$O(16) $= 100$ (2), $\angle$O(7)$\cdots$N(13)$\cdots$O(16) $= 70\cdot8$ (1)°]. This intermolecular hydrogen bond leads to slightly shortened intermolecular contact distances from O(7) to C(14) [$3\cdot142$ (3) Å] and to O(16) [$3\cdot289$ (3) Å]. All the other intermolecular approaches

are of the same magnitude as van der Waals contact distances.

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