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# The Crystal and Molecular Structure of 1,6-Dimethyl-4-oxo-1,6,7,8-tetrahydro-3-homopyrimidazolecarboxylic acid, $C_{11}H_{14}N_2O_3$

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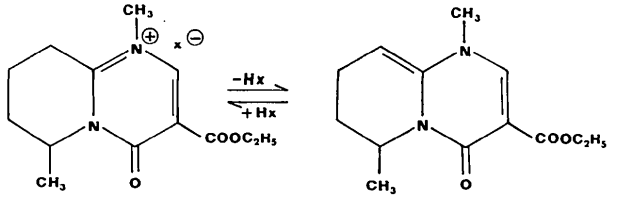
1,6-Dimethyl-4-oxo-1,6,7,8-tetrahydro-3-homopyrimidazolecarboxylic acid (DOTHPCA) crystallizes in the monoclinic space group $P2_1/n$ with $a=9{\cdot}112$, $b=9{\cdot}624$, $c=12{\cdot}407$ Å and $\beta=94{\cdot}8°$; $Z=4$. The phase problem was solved by direct methods, and the final atomic parameters were obtained by block-diagonal least-squares refinement; the final conventional $R=5{\cdot}54\%$ for all reflexions. The non-hydrogen atoms of the molecule with the exception of five atoms (three of these are ring atoms) are in one plane with a maximum deviation of 0·08 Å. The C-bonded methyl carbon atom is in an axial position and deviates from the plane in an opposite sense to the four other atoms which are also out of the plane. There is an intramolecular hydrogen bond with distances of 1·04 and 1·654 Å to the proton and an OHO angle of 144·4°.

## Introduction

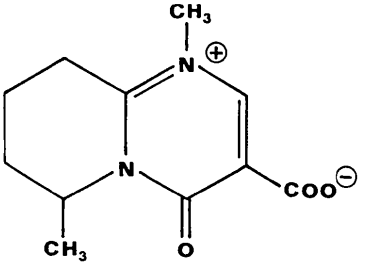
Among the homopyrimidazole derivatives, 1,6-dimethyl-3-carbethoxy-4-oxo-6,7,8,9-tetrahydrohomopyrimidazolium methyl sulphate, Probon$^R$, Chinoin (Negwer, 1971), was found to be a new analgesic drug. A crystal structure determination (Simon & Sasvári, 1975) showed that Probon$^R$ contains a tertiary and a quaternary nitrogen atom. As analgesic action can be enforced under physiological conditions by a form containing only tertiary nitrogens, it is believed that Probon$^R$ does not act directly but acts through one of its metabolites, *i.e.*, in the living organism Probon$^R$ undergoes biological metabolism resulting in a tautomeric form with only tertiary nitrogens. A metabolite of Probon$^R$ in crystalline form was therefore sought in order to determine the conformation of this effective compound.

From earlier investigations (Mészáros, Knoll, Szentmiklósi, Dávid, Horváth & Hermecz, 1972) it had been verified that depending on *p*H the above ester (Probon$^R$) is capable of the following tautomeric transformation:



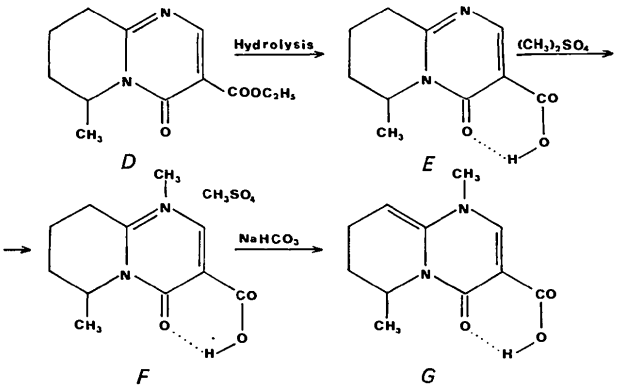

resulting in the form *B*, which satisfies the condition for only tertiary nitrogen atoms and shows analgesic activity under physiological conditions. The shift of double bond in *B* relative to *A* could be verified by n.m.r. investigation. Form *B*, which is in equilibrium with *A* with a concentration depending on the *p*H, could not be obtained in crystalline form. Therefore an attempt was made to reproduce the removal of Probon$^R$ in the living organism, which resulted in an active derivative that could be crystallized.

First it was assumed that ester hydrolysis takes place in the living organism. The free acid, obtained in this way, however, was found to be inactive; therefore a betain structure *C* was assumed for this product (Knoll, Magyar & Bánfi, 1971),




*C*

Later the pyrimidazole derivative *G* with only tertiary nitrogen atoms was successfully prepared in the following way:



The product *G*, which is identical with the title compound, has an analgesic activity and was thought to be the metabolite of Probon$^R$ directly causing the long-lasting analgesic effect in the organism.

So far, the title compound has not been obtained *in vitro* from Probon$^R$ in a crystalline modification. Recently it has been shown experimentally that during the alkaline hydrolysis of Probon$^R$ first by OH addition at C(10) (see Fig. 1), an intermediate compound is obtained from which further transformations may proceed in two directions, in one of which ring opening takes place at the C(10)–N(1) bond. This, and all its additional products are inactive. Most probably the earlier hydrolysis product assigned to *C* must be identical with that obtained immediately after ring opening. Control investigations carried out by one of the authors (Z.M.) are in progress. In the other direction mentioned, after OH addition, form *B* is obtained, the hydrolysis of which may result in form *G*. *G* could actually be found among the metabolites of Probon$^R$.

## Experimental

The crystals used for the present structure determination were crystallized from a solution in ethanol. They are yellow, rhomboid and elongated in one of the plane diagonals parallel to **a**.

The cell dimensions were determined from Buerger precession photographs taken around the three crystallographic axes with Cu $K\alpha$ radiation.

*Crystal data*

$a=9{\cdot}112$ (4), $b=9{\cdot}624$ (10), $c=12{\cdot}407$ (8) Å, $\beta=94{\cdot}8$ (1)°; $V=1084{\cdot}26$ Å$^3$; $F(000)=472$; $D_m=1{\cdot}360$ (pycnometer), $D_x=1{\cdot}362$ g cm$^{-3}$; $Z=4$; $\mu$(Cu $K\alpha$)$=7{\cdot}87$ cm$^{-1}$.

The space group $P2_1/n$ was determined from the systematic absences $h0l$ $h+l$ odd, $h00$, $0k0$ and $00l$ $h$, $k$ and $l$ odd. Intensities were measured by the equi-inclination procedure on a semi-automatic two-circle Stoe–Güttinger single-crystal diffractometer. The measurement and calculation of intensities was accomplished in the way described by Sasvári, Simon, Bognár & Makleit (1974). 56 reflexions with $I<2\sigma(I)$ were taken as unobserved out of a total of 1223 independent reflexions. The size of the crystal satisfied the condition $\mu R\leq 0{\cdot}3$ and no absorption correction was made.

After the Lorentz–polarization correction the absolute scale and approximate isotropic thermal parameter $B=3{\cdot}846$ Å$^2$ were determined by a Wilson plot using all the reflexion data.

## Determination of the structure

The phase problem was solved by direct methods, using $|E|$'s calculated from observed structure factor values in the conventional way. The *MULTAN* program of Main, Woolfson & Germain (1971) was used with local modifications on the ICL-1903A computer. Starting with $E$ values of 148 reflexions ($E\geq 1{\cdot}54$) and accepting 800 phase relationships with the highest $E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}$ values in a fully automatic operation, the program resulted in four probable phase sets from which that with the highest absolute figure of merit (ABSFOM = 1·1692) and lowest residual (27·67) gave the correct signs of all 148 reflexions. The $E$ map calculated with this sign combination revealed the peaks of all 16 non-hydrogen atoms. Some superfluous peaks in the $E$ map could be deleted on the basis of distance calculations. Atomic positions obtained from the $E$ map resulted in an $R$ of 0·285. For the calculation of the Fourier function the program of Domenicano & Vaciago (1966) was used.

The atomic parameters obtained were directly refined by the least-squares method with the program of Albano, Domenicano & Vaciago (1966) minimizing the function $\Phi=\sum_{\mathbf{h}} w_{\mathbf{h}}[F_{o\mathbf{h}}-(1/G)|F_{c\mathbf{h}}|]^2$, where $G$ is the

Table 1. *Final fractional coordinates* ($\times 10^4$) *and anisotropic thermal parameters* ($\times 10^4$) *for non-hydrogen atoms*

The estimated standard deviations are in parentheses. The $b_{ij}$ are defined by:

$$T=\exp\left[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)\right].$$

| | $x$ | $y$ | $z$ | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| O(12) | −1260 (2) | 1917 (2) | 804 (2) | 126 (3) | 86 (2) | 120 (2) | −29 (5) | −18 (4) | 17 (4) |
| O(13) | −3533 (2) | 1367 (2) | 202 (2) | 109 (3) | 133 (3) | 135 (2) | 49 (5) | −16 (4) | 77 (4) |
| O(17) | 501 (2) | 3 (2) | 1494 (2) | 89 (3) | 89 (2) | 93 (2) | −36 (4) | −26 (3) | −6 (3) |
| N(1) | −2826 (2) | −2757 (3) | 1103 (2) | 83 (3) | 99 (3) | 66 (2) | −43 (5) | −8 (4) | 20 (3) |
| N(5) | −293 (2) | −2228 (2) | 1543 (2) | 73 (3) | 79 (2) | 64 (2) | −2 (5) | −19 (3) | 4 (3) |
| C(2) | −3075 (3) | −1417 (3) | 848 (2) | 89 (4) | 99 (3) | 55 (2) | −7 (6) | 5 (4) | 7 (4) |
| C(3) | −1990 (3) | −445 (3) | 924 (2) | 73 (4) | 90 (3) | 56 (2) | 8 (6) | 0 (4) | −1 (4) |
| C(4) | −530 (3) | −850 (3) | 1324 (2) | 74 (4) | 87 (3) | 56 (2) | −14 (5) | 6 (4) | −12 (4) |
| C(6) | 1207 (3) | −2662 (3) | 1984 (2) | 77 (4) | 104 (3) | 73 (2) | 14 (6) | −25 (4) | 23 (4) |
| C(7) | 1554 (4) | −4083 (3) | 1526 (3) | 126 (5) | 104 (4) | 109 (3) | 52 (7) | 5 (6) | −4 (6) |
| C(8) | 425 (4) | −5157 (4) | 1824 (4) | 151 (5) | 102 (4) | 156 (4) | 21 (8) | −51 (7) | 8 (7) |
| C(9) | −1106 (4) | −4618 (3) | 1561 (3) | 136 (5) | 95 (3) | 96 (2) | −22 (7) | −32 (6) | 21 (5) |
| C(10) | −1392 (3) | −3258 (3) | 1406 (2) | 84 (4) | 86 (3) | 59 (2) | −25 (6) | −20 (4) | 8 (4) |
| C(11) | −2347 (3) | 992 (3) | 609 (2) | 83 (4) | 99 (3) | 78 (2) | 18 (6) | 10 (4) | 14 (4) |
| C(16) | 1294 (4) | −2624 (4) | 3214 (3) | 137 (5) | 170 (5) | 72 (2) | −22 (9) | −48 (6) | 14 (6) |
| C(18) | −4048 (3) | −3756 (4) | 996 (3) | 89 (4) | 137 (4) | 118 (3) | −100 (7) | −44 (6) | 60 (6) |

scaling factor. The weighting factor of Cruickshank (1961*a*), $w_h = 1/(a+bF+cF^2)$, was used with $a=4{\cdot}0$, $b=1$ and $c=0{\cdot}02$. Three cycles of refinement with isotropic and then three cycles with anisotropic thermal parameters reduced $R$ to 0·100 for the observed reflexions.

The difference function revealed all 14 hydrogen atoms. Two cycles of block-diagonal least-squares refinement, with anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for the 14 hydrogen atoms, resulted in the final $R=0{\cdot}053$ and 0·055 for observed and for all the reflexions, respectively. The final atomic parameters are summarized in Tables 1 and 2. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).*

Table 2. *Final fractional coordinates* ($\times 10^3$) *and isotropic thermal parameters* (Å$^2$) *of the hydrogen atoms*

Estimated standard deviations are in parentheses.

| | *x* | *y* | *z* | *B* |
|---|---|---|---|---|
| H(2) | −419 (4) | −113 (4) | 63 (3) | 3·1 (9) |
| H(6) | 190 (4) | −195 (4) | 166 (3) | 3·1 (8) |
| H(70) | 270 (4) | −434 (4) | 188 (3) | 4·7 (9) |
| H(71) | 149 (4) | −396 (4) | 68 (3) | 4·7 (10) |
| H(80) | 55 (5) | −534 (5) | 267 (4) | 7·0 (12) |
| H(81) | 63 (5) | −596 (5) | 140 (3) | 6·3 (11) |
| H(9) | −195 (4) | −526 (5) | 153 (3) | 5·0 (10) |
| H(12) | −29 (4) | 146 (4) | 103 (3) | 4·4 (9) |
| H(160) | 53 (4) | −329 (4) | 354 (3) | 4·7 (10) |
| H(161) | 236 (4) | −300 (4) | 355 (3) | 4·1 (9) |
| H(162) | 114 (4) | −172 (4) | 346 (3) | 3·8 (9) |
| H(180) | −499 (4) | −322 (4) | 75 (3) | 4·2 (8) |
| H(181) | −382 (5) | −455 (5) | 44 (4) | 6·9 (11) |
| H(182) | −418 (5) | −416 (5) | 176 (3) | 5·9 (11) |

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30909 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

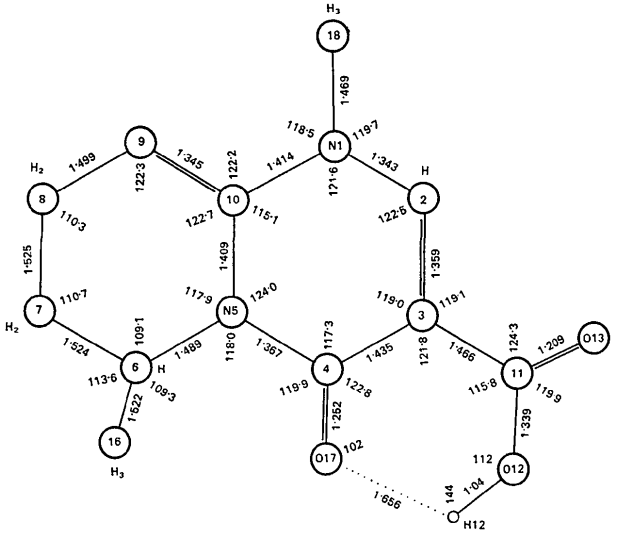



Fig. 1. Schematic drawing of the molecule with atom numbering and bond lengths and angles.

## The geometry of the molecule

A schematic drawing of the molecule with atomic numbering can be seen in Fig. 1. The non-hydrogen atoms of the molecule with the exception of C(7), C(8), C(9), C(16) and O(13) are coplanar with a maximum deviation of 0·08 Å. The C(16) methyl carbon atom is in an axial position to the plane and deviates from it in an opposite sense to the other non-hydrogen atoms which are out of the plane. The plane constants and atomic deviations from the plane are given in Table 3. The bond lengths and angles can be seen in Tables 4 and 5.

Table 3. *Least-squares plane of the molecule with atomic deviations*

The plane constants ($Ax+By+Cz=D$) are referred to crystal axes and coordinates in Å.

$A=0{\cdot}29279$ $B=0{\cdot}17359$ $C=0{\cdot}96141$ $D=1{\cdot}58321$

| | | | | |
|---|---|---|---|---|
| Atoms forming the plane | | | | |
| N(1), C(2), C(3), C(4) | 0·0258 | 0·0120 | −0·0245 | −0·0045 |
| N(5), C(6), C(10), C(11) | −0·0367 | 0·0166 | −0·0790 | −0·0649 |
| O(12), O(17), C(18) | 0·0322 | 0·0657 | 0·0573 | |
| Atoms not forming the plane | | | | |
| C(7), C(8), C(9), O(13) | −0·8597 | −0·3824 | −0·1976 | −0·1713 |
| C(16) | 1·4669 | | | |

Table 4. *Bond lengths* (Å) *and their estimated standard deviations in parentheses*

| | | | |
|---|---|---|---|
| N(1)—C(2) | 1·343 (4) | C(2)—H(2) | 1·07 (4) |
| N(1)—C(10) | 1·414 (4) | C(6)—H(6) | 1·03 (4) |
| N(1)—C(18) | 1·469 (4) | C(7)—H(70) | 1·12 (4) |
| C(2)—C(3) | 1·359 (4) | C(7)—H(71) | 1·06 (4) |
| C(3)—C(4) | 1·435 (4) | C(8)—H(80) | 1·06 (5) |
| C(3)—C(11) | 1·466 (4) | C(8)—H(81) | 0·97 (4) |
| C(4)—N(5) | 1·367 (3) | C(9)—H(9) | 0·98 (4) |
| C(4)—O(17) | 1·252( 3) | O(12)–H(12) | 1·01 (4) |
| N(5)—C(6) | 1·489 (4) | C(16)–H(160) | 1·06 (4) |
| N(5)—C(10) | 1·409 (3) | C(16)–H(161) | 1·09 (4) |
| C(6)—C(7) | 1·524 (4) | C(16)–H(162) | 0·94 (4) |
| C(6)—C(16) | 1·522 (5) | C(18)–H(180) | 1·02 (4) |
| C(7)—C(8) | 1·525 (5) | C(18)–H(181) | 1·06 (5) |
| C(8)—C(9) | 1·499 (5) | C(18)–H(182) | 1·04 (4) |
| C(9)—C(10) | 1·345 (4) | | |
| C(11)–O(12) | 1·339 (4) | Intramolecular distance (Å) | |
| C(11)–O(13) | 1·209 (4) | O(17)–H(12) | 1·656 (4) |

## Thermal motion analysis

The r.m.s. amplitudes and vectors of the principal axes of the thermal vibration ellipsoids of the non-hydrogen atoms are listed in Table 6. The molecule with thermal vibration ellipsoids can be seen in Fig. 2. [*ORTEP*, Johnson (1965)], projected in a direction parallel to (010) and inclined to the crystal axis *a* at an angle of 60°.

The thermal motion of the molecule has been analysed in terms of rigid-body vibration on the basis

Table 5. *Bond angles* (°) *and their estimated standard deviations in parentheses*

| | | | |
|---|---|---|---|
| C(2)—N(1)–C(10) | 121·6 (2) | N(5)—C(6)—C(7) | 109·1 (2) |
| C(2)—N(1)–C(18) | 119·7 (2) | N(5)—C(6)—C(16) | 109·3 (2) |
| C(10)–N(1)–C(18) | 118·5 (2) | C(7)—C(6)—C(16) | 113·6 (3) |
| N(1)—C(2)–C(3) | 122·5 (3) | C(6)—C(7)—C(8) | 110·7 (3) |
| C(2)—C(3)–C(4) | 119·0 (2) | C(7)—C(8)—C(9) | 110·3 (3) |
| C(2)—C(3)–C(11) | 119·1 (2) | C(8)—C(9)—C(10) | 122·3 (3) |
| C(4)—C(3)–C(11) | 121·8 (2) | N(1)—C(10)–N(5) | 115·1 (2) |
| C(3)—C(4)–N(5) | 117·3 (2) | N(1)—C(10)–C(9) | 122·2 (3) |
| C(3)—C(4)–O(17) | 122·8 (2) | N(5)—C(10)–C(9) | 122·7 (3) |
| N(5)—C(4)–O(17) | 119·9 (2) | C(3)—C(11)–O(12) | 115·8 (2) |
| C(4)—N(5)–C(6) | 118·0 (2) | C(3)—C(11)–O(13) | 124·3 (3) |
| C(4)—N(5)–C(10) | 124·0 (2) | O(12)–C(11)–O(13) | 119·9 (3) |
| C(6)—N(5)–C(10) | 117·9 (2) | O(12)–H(12)–O(17) | 144·4 |
| N(1)—C(2)–H(2) | 116·4 (2·0) | C(8)—C(9)—H(9) | 120·2 (2·5) |
| C(3)—C(2)–H(2) | 121·0 (2·0) | C(10)—C(9)—H(9) | 117·5 (2·5) |
| N(5)—C(6)–H(6) | 104·0 (2·0) | C(11)—O(12)–H(12) | 112·3 (2·2) |
| C(7)—C(6)–H(6) | 107·5 (2·0) | C(6)—C(16)–H(160) | 113·1 (2·2) |
| C(16)–C(6)–H(6) | 112·8 (2·0) | C(6)—C(16)–H(161) | 110·5 (2·0) |
| C(6)—C(7)–H(70) | 105·3 (2·0) | C(6)—C(16)–H(162) | 110·3 (2·3) |
| C(6)—C(7)–H(71) | 105·7 (2·2) | H(160)–C(16)–H(161) | 104·3 (2·9) |
| C(8)—C(7)–H(70) | 112·3 (2·9) | H(160)–C(16)–H(162) | 108·4 (3·2) |
| C(8)—C(7)–H(71) | 109·7 (2·2) | H(161)–C(16)–H(162) | 110·1 (3·0) |
| H(70)–C(7)–H(71) | 113·0 (2·0) | N(1)—C(18)–H(180) | 107·8 (2·0) |
| C(7)—C(8)–H(80) | 109·5 (2·5) | N(1)—C(18)–H(181) | 110·1 (2·4) |
| C(7)—C(8)–H(81) | 104·3 (2·6) | N(1)—C(18)–H(182) | 107·8 (2·4) |
| C(9)—C(8)–H(80) | 106·9 (2·5) | H(180)–C(18)–H(181) | 111·8 (3·2) |
| C(9)—C(8)–H(81) | 112·1 (2·6) | H(180)–C(18)–H(182) | 107·4 (3·1) |
| H(80)–C(8)–H(81) | 113·8 (3·6) | H(181)–C(18)–H(182) | 111·7 (3·4) |

Table 6. *Principal axes of the thermal vibration ellipsoids for non-hydrogen atoms given by their lengths* (Å) *and vectors referred to crystal axes*

The origins of principal axes are considered to be at the site of the corresponding atom and vector components are given in fractions ($\times 10^3$).

| | $i$ | $U_i$ (Å) | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|
| N(1) | 1 | 0·246 | −292 | −260 | 124 |
| | 2 | 0·208 | −289 | −262 | 98 |
| | 3 | 0·171 | −299 | −284 | 108 |
| C(2) | 1 | 0·219 | −303 | −161 | 77 |
| | 2 | 0·205 | −304 | −131 | 71 |
| | 3 | 0·191 | −287 | −140 | 90 |
| C(3) | 1 | 0·210 | −194 | −38 | 77 |
| | 2 | 0·205 | −197 | −24 | 98 |
| | 3 | 0·173 | −180 | −47 | 96 |
| C(4) | 1 | 0·215 | −51 | −98 | 147 |
| | 2 | 0·199 | −60 | −69 | 141 |
| | 3 | 0·173 | −71 | −91 | 129 |
| N(5) | 1 | 0·231 | −21 | −225 | 137 |
| | 2 | 0·193 | −29 | −203 | 153 |
| | 3 | 0·167 | −12 | −223 | 160 |
| C(6) | 1 | 0·252 | 127 | −275 | 180 |
| | 2 | 0·219 | 129 | −246 | 194 |
| | 3 | 0·166 | 137 | −270 | 204 |
| C(7) | 1 | 0·292 | 159 | −405 | 130 |
| | 2 | 0·249 | 176 | −392 | 157 |
| | 3 | 0·198 | 170 | −424 | 154 |
| C(8) | 1 | 0·361 | 54 | −516 | 155 |
| | 2 | 0·244 | 66 | −505 | 189 |
| | 3 | 0·213 | 52 | −536 | 185 |
| C(9) | 1 | 0·293 | −125 | −456 | 176 |
| | 2 | 0·223 | −132 | −458 | 146 |
| | 3 | 0·206 | −116 | −483 | 157 |
| C(10) | 1 | 0·232 | −151 | −317 | 155 |
| | 2 | 0·199 | −142 | −308 | 133 |
| | 3 | 0·171 | −156 | −332 | 135 |
| C(11) | 1 | 0·249 | −236 | 93 | 41 |
| | 2 | 0·216 | −227 | 120 | 57 |
| | 3 | 0·183 | −216 | 93 | 63 |
| O(12) | 1 | 0·312 | −134 | 196 | 104 |
| | 2 | 0·229 | −149 | 200 | 74 |
| | 3 | 0·194 | −134 | 173 | 80 |
| O(13) | 1 | 0·340 | −351 | 123 | −5 |
| | 2 | 0·250 | −337 | 156 | 16 |
| | 3 | 0·188 | −337 | 126 | 25 |
| C(16) | 1 | 0·291 | 143 | −286 | 312 |
| | 2 | 0·267 | 145 | −245 | 310 |
| | 3 | 0·199 | 145 | −262 | 333 |
| O(17) | 1 | 0·277 | 42 | 1 | 170 |
| | 2 | 0·216 | 38 | 19 | 145 |
| | 3 | 0·171 | 35 | −9 | 146 |
| C(18) | 1 | 0·335 | −416 | −359 | 121 |
| | 2 | 0·243 | −414 | −357 | 88 |
| | 3 | 0·156 | −420 | −383 | 98 |

of Cruickshank's (1961*b*) procedure, with the program of Schomaker & Trueblood (1968). By comparing U tensors of the individual non-hydrogen atoms calculated from the rigid-body thermal vibration ($U_{calc}$) and derived from the structure analysis ($U_{obs}$), a satisfactory agreement can be obtained (Table 7), which supports the rigid-body assumption, if only that part of the molecule excluding C(7), C(8) and C(9) of the left hand ring and the COOH group on the right hand ring is taken as the rigid body.

The translational and librational tensors of the assumed rigid-body portion of the molecule are given in Table 8. The principal axes of the same tensor ellipsoid can be seen in Table 9.

## Discussion of the structure

By hydrolysis, the $C_2H_5$ group and one H atom on C(9) in Probon$^R$ (Simon & Sasvári, 1975) are split from the molecule, and accordingly the N(1)–C(10) double bond (1·351 Å) changes to a single bond with a length of 1·414 Å, and the positive charge of N(1) disappears. At the same time, a new double bond is formed at C(9)–C(10) with a length of 1·345 Å. With this shift of double bond, the bond lengths around the N(5) atom are rearranged in such a way that N(5)–C(10) is increased from 1·312 to 1·409 Å and N(5)–C(4) decreased from 1·450 to 1·367 Å. The bond-length rearrangement around N(5) is very similar to that found in the homopyrimidazole derivative $C_{12}H_{16}N_2O_3$ (Sasvári & Simon, 1973) in the sense that the average N(5)–C bond length of 1·422 Å is, within one deviation (0·004 Å), the same as in the $C_{12}H_{16}N_2O_3$ molecule (1·426 Å). In Probon$^R$, however, the average N(5)–C bond length is somewhat greater (1·434 Å) but still within $3\sigma$, and very near to the value of 1·438 Å found for the average of the same bond lengths in the homopyrimidazole derivative $C_{13}H_{20}N_2O_3$ (Simon & Sasvári, 1972). Owing to conjugation the shortening of N(5)–C(4) is accompanied by a lengthening of the C(4)=O(17) double bond from 1·208 Å (in Probon$^R$) to 1·252 Å in the title molecule. All other bond lengths of the title molecule are approximately the same as in the other homopyrimidazole derivatives.

The left-hand ring of the title molecule (Fig. 1) is to some extent distorted with C(7), C(8) and C(9) out of the molecular plane with respectively decreasing deviations.

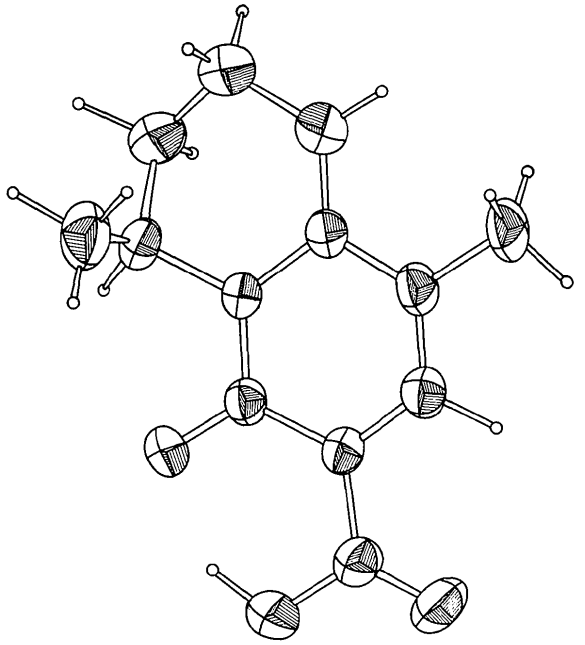


Fig. 2. Perspective view of the molecule in which the non-hydrogen atoms are represented by their thermal vibration ellipsoids.

Table 9. *Principal axes of the translational* **T** *and librational* **ω** *tensors of the atoms forming the rigid body*

The principal axes are given by their lengths and their unit vectors referred to an orthogonal axial system.

| Tensor | | $(u^2)^{1/2}$ | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|
| **T** | 1 | 0·204 (Å) | 0·277 | −0·961 | 0·027 |
| | 2 | 0·200 | 0·435 | 0·101 | −0·895 |
| | 3 | 0·139 | 0·857 | 0·259 | 0·446 |
| **ω** | 1 | 0·082 (rad) | 0·668 | −0·629 | 0·398 |
| | 2 | 0·057 | 0·736 | 0·477 | −0·481 |
| | 3 | 0·034 | 0·113 | 0·614 | 0·781 |

Table 7. *Observed and calculated components of the* **U** *tensors of individual non-hydrogen atoms referred to anorthogonal axial system (in* $10^{-2}$ Å$^2$)

The listed atoms form the part of the molecule assumed as the rigid body.

| | $U_{11}$ | | $U_{22}$ | | $U_{33}$ | | $U_{12}$ | | $U_{13}$ | | $U_{23}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | obs | calc | obs | calc | obs | calc | obs | calc | obs | calc | obs | calc |
| N(1) | 3·56 | 3·49 | 4·66 | 4·85 | 5·10 | 5·18 | −1·01 | −0·93 | −0·65 | −0·78 | 0·61 | 0·60 |
| C(2) | 3·74 | 3·00 | 4·64 | 4·94 | 4·28 | 4·32 | −0·16 | −0·34 | −0·23 | −0·30 | 0·21 | 0·36 |
| C(3) | 3·12 | 3·11 | 4·21 | 4·16 | 4·31 | 4·22 | 0·18 | 0·00 | −0·36 | −0·12 | −0·02 | −0·14 |
| C(4) | 3·13 | 3·24 | 4·08 | 3·94 | 4·36 | 4·54 | −0·28 | −0·28 | −0·20 | −0·59 | −0·36 | −0·31 |
| N(5) | 3·21 | 3·29 | 3·72 | 4·08 | 4·93 | 4·17 | −0·04 | −0·29 | −0·95 | −0·64 | 0·11 | 0·04 |
| C(6) | 3·38 | 3·66 | 4·88 | 4·99 | 5·67 | 5·72 | 0·25 | −0·16 | −1·18 | −1·21 | 0·69 | 0·66 |
| C(10) | 3·65 | 3·78 | 4·02 | 4·16 | 4·60 | 4·85 | −0·57 | −0·63 | −0·94 | −0·73 | 0·24 | 0·39 |
| C(11) | 3·50 | 3·78 | 4·64 | 4·34 | 6·07 | 6·31 | 0·37 | 0·49 | −0·21 | 0·11 | 0·42 | 0·21 |
| C(16) | 6·02 | 5·51 | 7·97 | 7·57 | 5·59 | 5·64 | −0·51 | −0·07 | −1·84 | −2·37 | 0·42 | 0·73 |
| O(17) | 3·91 | 3·91 | 4·17 | 4·23 | 7·20 | 7·14 | −0·79 | −0·65 | −1·34 | −1·40 | −0·18 | −0·32 |
| C(18) | 4·01 | 4·46 | 6·44 | 6·18 | 9·15 | 9·14 | −2·38 | −2·08 | −2·03 | −1·89 | 1·80 | 1·72 |

Table 8. *Translational* **T** ($10^{-2}$ Å$^2$) *and librational* **ω** ($10^{-2}$ rad$^2$) *tensors of the atoms (Table 7) which form the rigid body, referred to an orthogonal axial system*

The e.s.d.'s given in parentheses refer to the last two digits.

$$\mathbf{T} = \begin{pmatrix} 3{\cdot}17\ (11) & -0{\cdot}30\ (10) & -0{\cdot}43\ (11) \\ & 4{\cdot}06\ (12) & -0{\cdot}14\ (12) \\ & & 3{\cdot}76\ (15) \end{pmatrix} \qquad \boldsymbol{\omega} = \begin{pmatrix} 0{\cdot}48\ (05) & -0{\cdot}16\ (02) & 0{\cdot}08\ (03) \\ & 0{\cdot}38\ (04) & -0{\cdot}19\ (03) \\ & & 0{\cdot}25\ (03) \end{pmatrix}$$

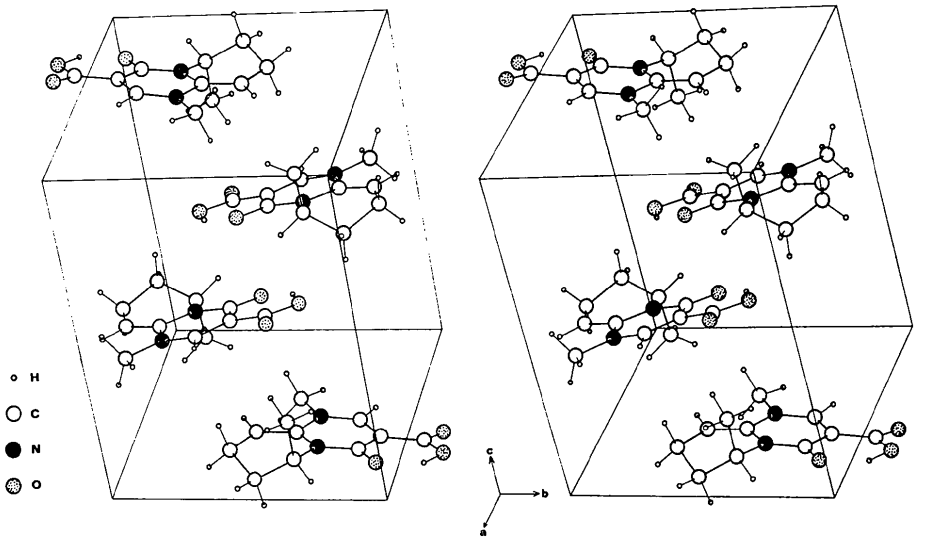



Fig. 3. Stereoscopic projection of the unit-cell contents down a direction deviating from the *b* axis by a rotation of the crystal about *z* and *x* by 33 and −21°, respectively.

An intramolecular hydrogen bond with a length of 2·696 Å has been found (Fig. 1). The three atoms of the O(12)–H(12)···O(17) hydrogen bond are, within one deviation (0·07 Å), in the plane of the molecule forming an (OHO) angle of 144·4°. Thus the hydrogen atom is significantly out of the O–O direction.

The spatial packing of the molecules in the crystal structure conforms to the molecular close packing. The shortest intermolecular atomic distances are given in Table 10. The stereographic view of the packing can be seen in Fig. 3. [*ORTEP*, Johnson (1965)].

Table 10. *Shortest intermolecular distances*

| From atom in $x,y,z$ | To atom | In position | Distance (Å) |
|---|---|---|---|
| H(2) | H(80) | $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ | 2·644 |
| H(2) | H(160) | $-\frac{1}{2}+x, -\frac{1}{2}-y, -\frac{1}{2}+z$ | 2·636 |
| H(70) | H(162) | $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$ | 2·575 |
| H(81) | H(12) | $x, -1+y, z$ | 2·645 |
| H(81) | H(161) | $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$ | 2·685 |
| H(12) | H(161) | $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ | 2·729 |
| H(162) | H(181) | $\frac{1}{2}+x, -\frac{1}{2}-y, \frac{1}{2}+z$ | 2·746 |
| H(180) | H(181) | $-1-x, -1-y, -z$ | 2·772 |
| H(181) | H(181) | $-1-x, -1-y, -z$ | 2·482 |

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